REREGISTRATION ELIGIBILITY SCIENCE CHAPTER

FOR

ATRAZINE

ENVIRONMENTAL FATE AND EFFECTS CHAPTER

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I. Environmental Risk Conclusions

Atrazine Concerns

Atrazine is a herbicide widely used on major food crops as well as non-crop areas across the U.S. In the environment, atrazine is mobile and found in surface water and is present in ground water in high use areas. In addition, it is persistent in surface and ground waters, with half-lives that may exceed one year in static bodies of water. In addition to exposure model predictions, extensive monitoring data show the widespread presence of atrazine and its degradates in both surface and ground water. Atrazine has been widely detected in air and rainfall samples in high use areas and also in areas far removed from regions of high use.

This widespread environmental exposure has serious implications when compared to ecotoxicological endpoints of concern. The preliminary ecological risk assessment indicated that risk quotients exceeded the levels of concern for chronic effects on mammals, birds, fish, aquatic invertebrates and non-target plants are possible at maximum and in some cases typical use rates. A refined risk assessment focusing on the aquatic environment and using the extensive exposure monitoring data as well as additional ecotoxicological data found in the open literature, resulted in concerns for adverse toxicological effects on freshwater and estuarine plants and their communities as well as indirect adverse effects on aquatic invertebrate and fish populations at monitored atrazine levels in surface waters.

II. Introduction

Chemical and Usage

Atrazine (6-chloro-N-ethyl-N-isopropyl-1, 3, 5-triazine-2, 4-diamine) has the second largest poundage of any herbicide and is widely used to control broadleaf and many other weeds, primarily in corn, sorghum and sugarcane. As a selective herbicide, atrazine is applied pre- and post-emergence.

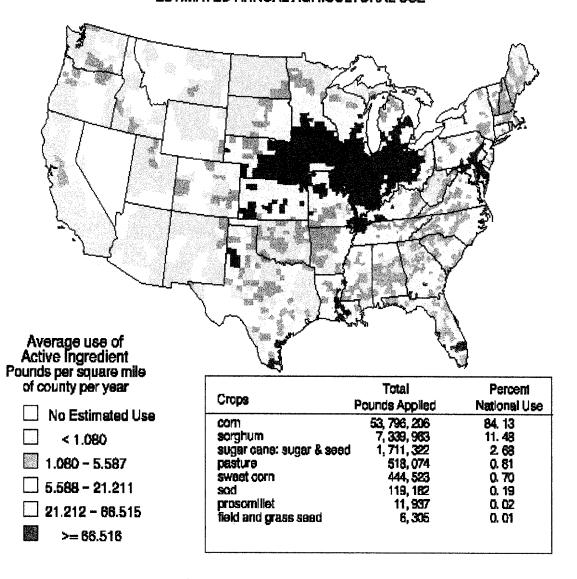
A national map of atrazine use per unit area is provided below. The map was downloaded from a U.S. Geological Survey (USGS), National Water Quality Assessment Program (NAWQA) website. The map is based upon the 1992 Census of Agriculture. The heaviest atrazine uses per unit area (those of > 66 lbs ai/sq mi of county/yr) occur in large portions of DE, IA, IL, IN, OH, and NE and in smaller portions of FL, KS, KY, LA, MD, MI, MN, MO, PA, TN, TX, and WI.

About 76 to 85 million lbs active ingredient (ai) of atrazine are produced annually. Atrazine is used on a variety of terrestrial food crops, non-food crops, forests, residential/industrial uses, golf course turf, recreational areas and rights-of-way. Atrazine yields season-long weed control in corn, sorghum and certain other crops. The major atrazine uses include: corn (83 percent of total ai produced per year - primarily applied pre-emergence), sorghum (11 percent of total ai produced), sugarcane (4 percent of total ai produced) and others (2 percent ai produced).

Atrazine formulations include dry flowable, flowable liquid, liquid, water dispersible granule, wettable powder and coated fertilizer granule. The maximum registered use rate for atrazine is 4 lbs ai/A; and 4 lbs ai/A is the maximum single, application rate for the following uses: sugarcane, forest trees (softwoods, conifers), forest plantings, guava, macadamia nuts, right-of-ways/fence rows/hedges, ornamental sod (turf farms), ornamental and/or shade trees, and Christmas trees.

About 60 million acres of total corn are treated with about 63 to 75 million lbs ai per year. The maximum label rates for corn are 0.84 to 3 lbs ai/A. The typical application rates on corn vary depending on the type and use for the corn, and are as follow: fresh sweet corn - 1.5 lbs ai/A (with 1 application on about 50 to 60 percent of the 220,000 acres), processed sweet corn - 0.9 lbs ai/A (with 1 application on about 58 to 65 percent of the 464,000 acres), and corn - 1.0 lbs ai/A (with an average of 1.1 applications on about 82 to 97 percent of the 72 million acres).

ATRAZINE ESTIMATED ANNUAL AGRICULTURAL USE



Sorghum is treated with about 8 to 12 million lbs ai per year on about 58 to 74 percent of the total 11 million US acres. The maximum label rates for sorghum are 1.3 to 3 lbs ai/A with a typical use rate of 1.1 lbs ai/A, averaging 1.1 applications per year for an average of 1.2 lbs ai/A/year.

Sugarcane is treated with about 2.5 to 5 million lbs ai per year on about 76 to 100 percent of the total 855 thousand US acres. The maximum, single application rates for sugarcane are 3.4 to 4 lbs ai/A with a typical use rate of 2.6 lbs ai/A, averaging 1.5 applications per year for an average of 3.9 lbs ai/A/year.

Other registered crop uses include: barley, guava, hay, macadamia nuts, oats, pasture, pineapples, rice, rye and winter wheat. Registered non-crop uses include uses on ornamental sod (farms), golf courses (turf), rangeland, residential lawns, Bermudagrass, grasses grown for seed, landscape maintenance, ornamental trees, forests, Christmas trees, recreational areas, rights-of-way, and industrial areas.

Mechanism of Action

Atrazine inhibits photosynthesis by stopping electron flow in Photosystem II.. Triazine herbicides associate with a protein complex of the photosystem II in chloroplast photosynthetic membranes (Schulz *et al.*, 1990). The result is an inhibition in the transfer of electrons which in turn inhibits the formation and release of oxygen.

Approach to Risk Assessment

EFED believes that the most important environmental risks associated with atrazine are adverse toxicological effects on freshwater and estuarine plants and their communities as well as indirect adverse effects on aquatic invertebrate and fish populations. Monitoring data suggest that atrazine concentrations in surface waters reach levels that could result in these effects, particularly in high use areas. However, EFED began with a preliminary ecological risk assessment based on a risk quotient analysis. From this analysis EFED used model simulations and registrant submitted data to conclude that risk quotients exceeding the levels of concern for chronic effects on mammals, birds, fish, aquatic invertebrates and non-target plants resulted for maximum and in some cases typical use rates. In addition to the data submitted by the registrant in support of registration, there existed a large body of toxicity data on aquatic organisms in the open scientific literature. These data included a number of aquatic microcosm, mesocosm and field studies showing adverse direct and indirect effects on aquatic systems. Unlike the results from the large number of laboratory studies available for atrazine, the results from these complex studies were expressed in terms of impacts on populations, communities and ecosystems and are not easily approached quantitatively, i.e., probabilistically.

In addition, there existed a relative abundance of surface water monitoring data for atrazine. However, these data were designed to assess the water-quality of the monitoring sites, not to establish exposure levels in aquatic habitat for comparison with aquatic ecotoxicity values. As

such they, too, were not amenable to a quantitative probabilistic analysis for aquatic exposure. However, with little robust monitoring data available for our exposure purposes, EFED chose a conservative approach by using the "available" maximum concentrations. EFED notes that there are some uncertainties with these maximum values. For example, all the monitoring sites were not sampled continuously on a daily basis; the sampling was not specifically designed to correspond to atrazine applications; the sampling was not specifically oriented to atrazine treatment areas. Consequently, if sampling missed a runoff event (i.e., a rainfall event) or if the site was spatially distant from atrazine applications, then the peak value would also have been missed. In effect, then, the conservative selection of the available maximum values is at least partially balanced by the low probability that the available maximum value represents the highest value due to a rainfall event.

Faced with a relatively large amount of both ecotoxicological data and monitoring data on atrazine; yet, also faced with the fact that the data did not appear to be appropriate for probabilistic analysis, EFED used the data in a refined deterministic risk assessment.

Coordination with EPA's Office of Water (OW)

The EPA's Office of Water (OW) is developing national ambient water quality criteria for protection of aquatic life for atrazine. Aquatic life criteria developed by OW are estimates of concentrations of a chemical in water that should not result in unacceptable adverse effects on aquatic organisms and their uses. When a decision is made that a national criterion is needed for a particular chemical, the Office of Water typically establishes two criteria (for fresh and salt water): a Criterion Continuous Concentration (CCC) and a Criterion Maximum Concentration (CMC). The CCC and CMC are generally estimates of the highest four-day average and one-hour average concentration, respectively, that should not result in unacceptable effects on aquatic organisms or their uses. Additional information related to OW's water quality criteria for atrazine can be found at center.water-resource@epa.gov.

To assess the potential risks to non-target aquatic life from use of pesticides, OPP generally uses the Quotient Method, a screening level assessment, whereby an Estimated Environmental Concentration (EEC) is divided by an effect level that is generally taken from a toxicity study submitted to EPA in connection with a pesticide's registration or reregistration. The result is a risk quotient (RQ) which is compared to a level of concern (LOC) for acute and chronic effects to non-target aquatic organisms.

Because the two approaches are different, OPP and OW are currently consulting on their respective methodologies. When the consultation is completed, there may be some modifications to these approaches which may result in some revisions to the final OPP and OW products. For additional details concerning the methods used by OW and OPP, refer to Appendix XV.

III. Integrated Environmental Risk Characterization

Summary of Major Risk Concerns

Considering atrazine's heavy and extensive use especially in agriculture, its widespread presence in surface and ground water, its adverse toxicological effects on freshwater and estuarine plants as well as its indirect effects on aquatic invertebrate and fish populations, continued atrazine use is likely to pose a risk to the health and integrity of some aquatic communities. These effects are most likely to occur in areas of high atrazine use where surface water contamination is likely to occur.

In addition, exposure through spray drift and runoff is likely to result in direct acute effects on many terrestrial plant species at both maximum and typical use rates. Incidents confirming damage to nontarget plants support this conclusion, and 1996-98 data from the American Association of Pest Control Operators (AAPCO) rank atrazine high among 58 pesticides confirmed to be involved in spray drift complaints.

Based on the initial screening-level assessment, direct acute effects on birds, mammals, fish and aquatic invertebrates are not expected at maximum use rates. However, chronic effects on mammals, birds, fish and aquatic invertebrates are possible at maximum and typical use rates. These conclusions are based on modeled exposure estimates combined with laboratory toxicity data. If risk managers require a refinement, extensive monitoring and field data are needed to permit a more detailed analysis confirming these potential adverse effects.

Terrestrial Risk Characterization (Birds and Mammals)

Terrestrial expected environmental concentrations (EECs) of atrazine to which birds and mammals were assumed to be exposed were estimated based on the highest value measured for foliar dissipation half-life from application of atrazine to turf in several locations throughout the southeastern United States. These foliar dissipation half-lives are most representative of atrazine used as a post-emergent herbicide applied directly to foliage of target plants. Atrazine is, however, used predominantly during crop pre-planting and pre-emergence and is, under these circumstances applied directly to soil rather than to foliage. As a result, EECs based on foliar dissipation half-life data, although indicative of post-emergent applications, are not representative of pre-plant and pre-emergence applications. Acute risks to mammals and birds were qualitatively assessed from EECs that were based on the maximum foliar dissipation halflife of 17 days obtained from foliar dissipation studies conducted in the southeastern United States. The ratio of the peak day-0 EECs to the LC50 values corresponding to the highest toxicities for mammals and birds indicate that the resulting risk quotients (RQs) are far less than Levels of Concern (LOCs), thereby indicating negligible potential for acute risks to birds. The risk quotients for small mammals exceed the LOCs for restricted use (RQ=0.2) and endangered species (RQ=0.1).

EFED's screening-level assessment suggests the potential for adverse chronic effects to

mammals and birds from atrazine applied at typical and maximum labeled rates. Estimated residues on terrestrial food items exceed EFED's levels of concern for chronic effects based on NOAELS of 50 and 10 ppm for rats and 225 ppm NOAELs for birds. The 10 ppm level is the NOAEL for adverse effects on second-generation pup body weights. Estimated residues on food items also exceed the 50 ppm NOAEL for adverse effects on reduced body weight and food consumption in adult rats. The mammalian reproductive NOAELs of 50 and 10 ppm are exceeded for 54 and 94 days, respectively, for maximum residue levels on short grass when foliar dissipation is considered. At the typical use rate for sugarcane (2.6 lbs ai/A), the duration of exceedence is 61 and 100 days, respectively.

As with mammals, the screening-level assessment suggests that there is the potential for adverse impacts on avian reproduction from maximum and typical application rates. At 675 ppm, the adverse effects noted for bobwhite quail include 29% reduction in egg production, a 67% increase in defective eggs, a 27% reduction in embryo viability, a 6 to 13% reduction in hatchling body weight, and a 10 to 16% reduction in 14-day old bobwhite body weight (Pedersen and DuCharme, 1992). At 675 ppm, an exposure level less than the modeled value for the maximum application rate on short grass (960 ppm), adverse effects on mallards included reductions of 49% in egg production and 61% in egg hatchability (Pedersen and DuCharme, 1992). At the typical corn use rate (1.1 lbs ai/A), the LOC is exceeded for about 4 days.

It is important to consider, however, that exposure of birds and mammals to atrazine applied as a pre-plant or pre-emergent herbicide is primarily a result of ingestion of earthworms and other soil organisms that can serve as a food source as well as from inadvertent ingestion of soil. Methods are not available to determine the levels of atrazine that could occur in soil and in earthworms and other soil organisms that are used as food sources by birds and mammals. The resulting levels of atrazine in soil and soil organisms that can serve as a source of food for birds and mammals are, however, expected to be considerably lower than estimated levels estimated to be present in plants used as food sources as a result of the dilution effect resulting from distribution of atrazine at and within one to three inches below the soil surface. Although risk quotients based on EECs from maximum foliar dissipation half-life data indicates that LOCs for chronic risks are exceeded, these risk quotients are over-estimates for birds and mammals that are exposed from ingestion of soil organisms and for birds and mammals exposed to habitats adjacent to the field that have atrazine levels on plants as a result of drift.

Historically, herbicides have had a much different effect on animal populations than insecticides. Insecticides generally affect animal populations acutely (e.g., carbofuran, chlorpyrifos, guthion, etc.) and/or severe reproductive impairment (e.g., DDT/DDE). If the insecticide-treated area is favorable habitat for one or more species, following the death of the resident species, other animals may quickly reoccupy the treated site and may or may not also succumb to poisoning from the pesticide.

Herbicide effects on wildlife are not normally acute in nature. Rather, the herbicide can alter the types of vegetation or reduce food sources in the habitat such that the animal must move elsewhere and possibly to a less suitable area. Thus, herbicides affect animal populations by

reducing favorable habitat and increasing competition among species for nesting and food resources. Inasmuch as essential vegetation in treated areas, such as right-of-ways, field margins and riparian areas are affected by spray drift and/or runoff, some bird and/or small mammal species may be forced to seek new areas for feeding, nesting and survival.

Terrestrial Risk Characterization (Plants)

Atrazine applications to crop and non-crop areas pose an exposure to non-target plants in areas adjacent to treated fields via spray drift and runoff. EFED's screening-level assessment for nontarget plants, which uses standard values for runoff and drift and compares exposure values to EC₂₅ values for tested species, suggests that atrazine poses risk to a wide range of nontarget species. Although only crop species are tested, the results are assumed to represent a range of wild plants. These plants may serve as habitat and/or a food source for birds, mammals beneficial insects and other organisms. Non-target terrestrial plants in adjacent fields or habitats are potentially at risk from spray drift and from runoff for all registered uses. The level of concern for endangered terrestrial plant species is exceeded for both monocots and dicots, with greater concern evident for higher application rates. The assessment also indicates concern for endangered plant species growing in areas adjacent to atrazine-treated fields from combined spray drift and runoff.

The assessment resulted in exceedences for ground and aerial applications of atrazine at typical and maximum labeled rates. The assessment suggests that three out of the ten tested crops (cucumber, soybeans, and cabbage) are at risk when spray drift alone is considered. The combination of spray drift and runoff poses risks to eight out of the ten crops if grown in dry habitats and to nine out of ten crops if grown in low-lying, semi-aquatic habitats. The screening-level assessment assumes that wetter habitats are at greater risk because they would receive a greater runoff load than would drier areas.

Aquatic Refined Risk Assessment

A substantial amount of monitoring data were available for freshwater streams, lakes, reservoirs, and estuarine areas. In addition, a large number of laboratory, microcosm, mesocosm, and actual field studies were found in the literature showing that atrazine concentrations measured in the environment reach levels that are likely to have negative impact on sensitive aquatic species and communities. These data provide a strong basis for concluding that the continued use of atrazine is likely to result in adverse effects on some aquatic communities.

The availability of these surface water monitoring data and laboratory and field study effects data provide the information needed for a refined risk assessment. Thus, this refined assessment will focus on the risk associated with atrazine contamination of freshwater streams, lakes, and reservoirs and estuaries, tidal ponds and marshes. The final conclusions are based on multiple lines of evidence that point to a greater likelihood of risk to some aquatic communities than indicated in the preliminary risk assessment using risk quotients. There is greater certainty of EFED's risk conclusions for aquatic systems for atrazine than for most other herbicides because

of the extensive monitoring and effects data.

Atrazine Exposure Characterization (General)

Atrazine is persistent in soil, with a half-life (time until 50% of the parent atrazine remains) exceeding 1 year under some conditions (Armstrong *et al.*, 1967). Studies on agricultural soils (Sirons *et al.* 1973; Dao *et al.* 1979) indicate that deethylated atrazine could account for extended toxicity in agricultural soils from one year to the next.

Atrazine is a mobile pesticide which can be transported via spray drift and runoff to surface water, and can leach to ground water. Davies et al. (1994) found that atrazine residues in ground water following a forest application may seep into adjacent Tasmanian surface waters, resulting in prolonged exposures to low levels of atrazine. Atrazine concentration in the small seepage ranged from 0.8 to 68 Fg/L during the two months after spraying. Atrazine concentrations in the Tasmanian stream peaked at 22 Fg/L the day of treatment and decreased with time from the day of spraying from a median of 8.1 Fg/L to a median of 0.3 Fg/L 13 to 15 months after spraying. Peak runoff of pesticides occurs when a severe storm closely follows application on sloping land (Baker et al. 1985; Frank et al. 1982; Moody and Goolsby 1993; Wauchope, 1978; Wauchope and Leonard, 1980; Wu et al. 1983). Maximum bulk concentrations of atrazine in runoff in the low milligrams per liter range have been documented (Hall et al. 1972; Kadoum and Mock, 1978; Roberts et al. 1979). Once runoff reaches adjacent surface waters, such as streams, rivers, ponds or lakes, the concentrations are diluted and the maximum concentrations of atrazine reported in the literature are typically in the low microgram per liter range (Richard et al. 1975. Frank and Sirons, 1979; Wu, 1981). One or more applications closely followed by successive rainfall/runoff events, however, can result in "pulsed" dosing and higher concentrations that are evident in the monitoring data Maximum atrazine concentrations in runoff and surface waters reported in selected references include: 4,700 Fg/L in bulk field runoff at the edge of a treated field (Wauchope 1978), 87.1 Fg/L in a survey of 12 streams in northwest Ohio (Baker et al. 1981), 32.8 Fg/L in a survey of 11 streams in Ontario (Frank and Sirons 1979), 26.0 Fg/L in a survey of 92 streams entering Great Lakes (Frank et al. 1979), 69.44 Fg/L (water) and 95.19 Fg/L (bottom sediment) in 5 rivers flowing into Lake Erie (Waldron 1974), 26.9 Fg/L in 5 Quebec rivers (Muir et al. 1978), 10 Fg/L in 9 central European rivers (Hörmann et al. 1979), 42 Fg/L in rivers and reservoirs in Iowa and Louisiana (Richard et al. 1975), and 1.0 Fg/L in the estuarine waters of the Rhode River estuary in Maryland (Wu 1981). Frank et al. (1979) reported that 77 percent of the samples from Canadian streams entering the Great Lakes were contaminated with atrazine. Given its persistence, mobility and wide use, atrazine contamination is widespread in the U.S.

Atrazine enters the atmosphere via volatilization and spray drift and is aerially deposited (a source of importance to some water bodies). About 25 percent of the atrazine entering Lake Michigan is from aerial deposition (Lake Michigan Mass Balance Study, 1999). Atrazine concentrations in rainfall samples taken in 1996 in the Lake Michigan Study were 2.8 Fg/L, which are similar to the atrazine concentrations (up to 2.9 Fg/L) in rainfall reported in Minnesota (Capel *et al.* 1994).

A recent study reports that atrazine was detected in more than 60% of weekly rainfall samples taken in 1995 from agricultural and urban sites in Mississippi, Iowa, and Minnesota (Majewski *et al.*, 2000). Similarly, air samples taken from agricultural sites in 1995 showed positive detections of atrazine in more than 80% of samples from IA, 60% of samples from MS, and in about 50% of samples from MN. Urban sites in MN and IA had a slightly lower frequency of atrazine detections in rainfall compared to agricultural sites, while in MS about 30% of the urban samples had positive detections (Foreman *et al.*, 2000). These studies also reported that atrazine was detected in 35% of rainfall samples and in 76% of air samples taken at a background site in Michigan located far from agricultural and urban areas. These data indicate that atrazine is transported through the atmosphere.

Atrazine Effects Characterization (General)

The data strongly suggest that atrazine will have direct negative impact on freshwater and estuarine plants as well as indirect effects on aquatic invertebrate and fish populations which rely on vegetative habitat for predator avoidance and sensitive organisms that are lower in the food chain. Concentrations of atrazine measured in surface waters suggest that negative impacts on aquatic ecosystems are occurring, particularly in areas of high atrazine use.

In general, atrazine is not very acutely toxic to aquatic animals. The most sensitive freshwater species tested are the rainbow trout 96-hour LC_{50} (5.3 mg/L) and the midge (*Chironomus tentans*) 48-hour LC_{50} 0.72 mg/L. The most sensitive estuarine/marine animals tested are the spot (*Leiostomus xanthurus*) 96-hour LC_{50} (8.5 mg/L) and the copepod (*Acartia tonsa*) 96-hour LC_{50} (88 ug/L). With rare exceptions, reported and modeled surface water concentrations of atrazine are considerably lower than these acute toxicity values. Suspended sediments had little effect on moderating the toxicity of atrazine to *Daphnia pulex* (Hartman & Martin 1985).

The most sensitive chronic NOAEC toxicity values for aquatic animals are 65 Fg/L for the brook trout, 60 Fg/L for the scud (*Gammarus fasciatus*) in freshwater, 1,900 Fg/L for sheepshead minnow (*Cyprinodon variegatus*) and 80 Fg/L for the mysid shrimp (*Mysidopsis bahia*). The sheepshead minnow acute 96-hour LC_{50} is greater than 16 mg/L with 30 percent mortality. Estimating the chronic NOAEC toxicity value for the more acutely sensitive spot (*Leiostomus xanthurus*) using acute-to-chronic ratio, the NOAEC for spot would be a little less than 1 mg/L.

Atrazine inhibits photosynthesis by stopping electron flow in Photosystem II. It has a rapid effect on plants with an equilibrium between the plant and water attained in the vascular aquatic plant *Potamogeton perfoliatus* within one hour. Recovery of oxygen evolution in treated plants (5, 25 and 100 Fg/L) placed in atrazine-free water is rapid, with no significant differences from controls after two hours, but indications of residual photosynthetic depression persisted after the 77-hour recovery period (Jones *et al.*, 1986). Given the persistent atrazine concentrations in the ponds, uncertainty exists about the effect(s) on plant recovery which would occur following chronic energy losses via respiration for sensitive species during prolonged suppression of photosynthesis.

Giddings, et al., 2000, have reviewed microcosm and mesocosm data and concluded that no lasting ecological damage results from exposure of aquatic communities to atrazine concentrations below 50 ug/L. They appear to confine their concerns to biomass and primary productivity, and suggest that aquatic communities are resilient and will easily recover from atrazine contamination at 50 ug/L. In addition, they maintain that sensitive species would be replaced with less sensitive species with the same ecological function.

EFED comes to a significantly different conclusion after reviewing much of the same data. First, studies such as Kettle *et al.* 1987 provide quite a bit of evidence to the contrary - namely, that 20 ug/L of atrazine can result in extreme negative impacts on the aquatic communities. By limiting their concerns to biomass and primary productivity, Giddings *et al.* ignored species diversity, an essential element in determining community impacts. Recovery in communities is always uncertain and proof of it requires the collection of considerable species specific data, none of which has been referenced by the authors. Finally, EFED does not believe it is possible to perform a proper assessment of reproductive effects of atrazine on plants without the data from true plant reproductive studies, and again, such data has not been referenced by the authors. EFED also notes that there are inevitably other herbicides present in contaminated water bodies, whose combined effects would act to lower the effective levels at which individual chemicals such as atrazine cause impact. Consequently, EFED does not agree with the level of 50 ug/L as an NOAEC for community-based effects for atrazine.

Effects Endpoints for the Refined Assessment

The measurement and assessment endpoints of concern used in the refined risk assessment are listed below in Tables 1-3 for each of the three aquatic areas being characterized: (1) freshwater ponds, lakes and reservoirs; (2) freshwater streams; and, (3) estuaries, tidal ponds and estuarine marshes. When the assessment endpoint relies on a laboratory measurement, the word "estimated" is used to describe the endpoint; when it relies on a simulated field or field measurement, the term "likely" is used. The measurements supporting these endpoints often occur at concentrations considerably lower than those submitted by registrants, reviewed by EFED and used in the preliminary risk assessment.

These data were taken from a plethora of effects data available in the literature. They provide an expanded view of the effects of atrazine on aquatic organisms in the laboratory, in simulated field situations, and in actual field situations. They show effects of atrazine on additional non-target species, on aquatic populations and communities, and on ecosystems that were not captured in the typical registrant generated data for registration. They provide the basis for this refined aquatic risk assessment.

Table 1. Key Endpoints for the Lentic Freshwater Environment (e.g., reservoirs, lakes). The Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96- hours) LC50 = 5,300 Fg/L	Rainbow trout / Mortality	00024716 Beliles & Scott 1965	Fish Mortality Estimated to Occur at 53,000 Fg/L
	Lab	Chronic Fish (44- weeks) NOAEC = 65 Fg/L; LOAEC= 120 Fg/L; MATC= 88 Fg/L	Brook trout / [7.2 % red. mean length, 16 % red. mean body weight]	00024377 Macek et al. 1976	Reduction in Fish Growth Estimated to Occur at 88 Fg/L
	Field (mesocosms)	96% Reduction in # of Young Fish Occurred at 20 Fg/L (Caused by Loss of Food and Habitat)	Bluegill sunfish	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Fish Population Reduction Likely to Occur at 20 Fg/L due to Loss of Food and Habitat
Invertebrates	Lab	Acute Invertebrate (48-hour) $LC_{50} = 720 \text{ Fg/L}$	Midge / Mortality	00024377 Macek et al. 1976	Invertebrate Mortality Estimated to Occur at 720 Fg/L
	Lab	Chronic Invertebrate (48- hour) NOAEC = 60 Fg/L; LOAEC = 140 Fg/L; MATC = 92 Fg/L	Scud / [25 % red. in development of F ₁ to seventh instar]	00024377 Macek <i>et</i> <i>al.</i> 1976	Reduction in Invertebrate Populations Estimated to Occur at 92 Fg/L
Invertebrates	Field	59-65% Reduction in Daphnid population growth occurred at 10 Fg/L over 18-days	Daphnids	45087414 Lampert et al. 1989	Invertebrate Populations Likely to be Reduced at 10 Fg/L
Non- Vascular Plants	Lab	Acute Algae (1- week) EC ₅₀ = 1 F g/L	Four species [41-93% reduction in chlorophyll production]	00023544 Torres & O'Flaherty 1976	Reduction in Primary Production ¹ Estimated to Occur at 1 Fg/L
	Microcosm	23% Reduction in gross primary production 10 Fg/L (at day 2); recovery by day 7	phytoplankton	45087413 Johnson 1996	Reduction in Primary Production Estimated to Occur at 10 Fg/L
	Field	42% Reduction in phytoplankton biomass (at days 2-7) occurred at 20 F g/L	phytoplankton	45020011 DeNoylles <i>et al.</i> 1982	Reduction in Primary Production Likely to Occur at 20 Fg/L

¹Primary production is the rate at which energy is bound, or organic material is created by photosynthesis, per unit of the earth's surface per unit time (Whittaker, 1975. Communities and Ecosystems. MacMillan Publishers, NY, NY. 385 pp.).

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Vascular Plants	Lab	Acute (14-days) $EC_{50} = 37 \text{ F g/L}$	Duckweed [50% reduction in growth]	43074804 Holberg 1993	Reduction in Macrophytes Estimated to Occur at 37 Fg/L
	Mesocosm	60% Reduction of macrophyte vegetation occurred at 20 Fg/L; by May of following year, 95% Reduction of macrophytes	Macrophytes	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Reduction in Macrophytes (number & diversity) Likely to Occur at 20 Fg/L

Table 2. Key Endpoints for the Lotic Freshwater Environment (e.g., streams). The Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96- hours) LC50 = 5,300 Fg/L	Rainbow trout / Mortality	00024716 Beliles & Scott 1965	Fish Mortality Estimated to Occur at 53,000 Fg/L
	Lab	Chronic Fish (44-weeks) NOAEC = 65 Fg/L; LOAEC= 120 Fg/L; MATC= 88 Fg/L	Brook trout / [7.2 % red. mean length, 16 % red. mean body weight]	00024377 Macek et al. 1976	Reduction in Fish Growth Estimated to Occur at 88 Fg/L
Invertebrates	Lab	Acute Invertebrate (48-hour) LC ₅₀ = 720 F g/L	Midge / Mortality	00024377 Macek et al. 1976	Invertebrate Mortality Estimated to Occur at 720 Fg/L
	Lab	Chronic Invertebrate (48-hour) NOAEC = 60 Fg/L; LOAEC= 140 Fg/L; MATC= 92 Fg/L	Scud / [25 % red. in development of F ₁ to seventh instar]	00024377 Macek et al. 1976	Reduction in Invertebrate Populations Estimated to Occur at 92 Fg/L

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Invertebrates	Stream	Significant Increase in daytime and nighttime invertebrate drift occurred at 22 F g/L due to increased predation	various species of stream dwelling invertebrates	45020003 Davies et al. 1994	Invertebrate Populations Likely to be Reduced at 22 Fg/L
Non-Vascular Plants	Lab	Acute Algae (1-week) EC ₅₀ = 1 F g/L	Four species [41-93% reduction in chlorophyll production]	00023544 Torres & O'Flaherty 1976	Reduction in Primary Production Estimated to Occur at 1 Fg/L
	Stream (first order adjacent to corn field in Canada)	79% (mean) Reduction in Total Phytoplankton Counts at 2.62 Fg/L (mean; range = 0.211 - 13.9)	phytoplankton	45020008 Lakshinarayana, O'Neill, Johnnavithula, Leger and Milburn, 1992	Reduction in Primary Production Likely to Occur at 2.62 Fg/L
Vascular Plants	Lab	Acute (14- days) $EC_{50} =$ 37 Fg/L	Duckweed [50% reduction in growth]	43074804 Holberg 1993	Reduction in Macrophytes Estimated to Occur at 37 Fg/L

Table 3. Key Endpoints for the Estuarine/Marine Environment (e.g., estuaries, tidal, marshes). Endpoints Chosen for Use in the Refined Risk Assessment are Highlighted.

<u> </u>			efined Risk Asse		1
Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96- hours) LC50 = 2,000 Fg/L	Sheepshead minnow / Mortality	45208303 Hall <i>et al</i> . 1994	Fish Mortality Estimated to Occur at 2,000 Fg/L
	Lab	Chronic Fish NOAEC = 1,900 Fg/L; LOAEC= 3400 Fg/L; MATC= 2542 Fg/L	Sheepshead minnow [89 % red. Juv. survival]	45202920 Ward & Ballantine 1985	Reduction in Fish Populations Estimated to Occur at 2542 F g/L
Invertebrates	Lab	Acute Invertebrate LC ₅₀ = 94 F g/L	Copepod (Acartia tonsa)	45202920 Ward & Ballantine 1985	Invertebrate Mortality Estimated to Occur at 94 Fg/L
	Lab	Chronic Invertebrate NOAEC = 80 Fg/L; LOAEC= 190 Fg/L; MATC= 123 Fg/L	Mysid [37 % red. Adult survival]	45202920 Ward & Ballantine 1985	Reduction in Invertebrate Populations Estimated to Occur at 123 Fg/L
Non-Vascular Plants	Lab	Acute (120- hours) Algae LC ₅₀ = 22 F g/L	Algae (Chrysophyceae; Isochrysis galbana)	41065204 Parrish 1978	Marine/Estuarine Algae Mortality Estimated to Occur at 22 Fg/L
	Field	Up to 50% reduction in primary production (days 3-11); up to 70% reduction in chlorophyll occurred at 0.12 Fg/L (similar effects also occurred at 0.56 and 5.8 lg/L) over 15-days	phytoplankton	45020021 Bester et al. 1995	Reduction in Primary Production Likely to Occur at 0.12 Fg/L
Vascular Plants	Lab	Significant reduction in dry weight occurred at 10 F g/L (calculated MATC from NOAEC=7.5 and LOAEC=14.3)	Sago Pondweed	[MRID pending] Chesapeake Bay Program 1998	Reduction in Macrophytes Estimated to Occur at 10 Fg/L

Key Group of Non-target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Microcosm	16% Reduction in Tuber formation; 55% Reduction in Biomass over reproductive season at 4 Fg/L	Wild Celery (Vallisneria Americana)	45020001 Cohn 1985	Reduction in Macrophytes Likely to Occur at 4 F g/L

Exposure Characterization (Pond)

In order to assess aquatic exposure to ponds under both maximum and typical use rate conditions, EFED implemented the refined tier II approach using the PRZM/EXAMS models. The upper tenth percentile concentration values, expressed in ppb (Fg/L), are summarized below. The results of three uses, corn, sugarcane, and sorghum, were based on the standard scenarios provided by EFED's Water Quality Tech Team (WQTT) to predict reasonable high exposure values, i.e., soils with high runoff potential and heavy rainfall amounts, for both maximum and typical use rates.

Treated Crop	Use Rate	Atrazine EEC Values ppb (Fg/L)					
	(lb ai/A)	Peak Conc.	96-hour Average	21-day Average	60-day Average	90-day Average	
Sugarcane	4.0	205	204	202	198	194	
	2.6	133	133	131	129	126	
Corn	2.0	38.2	38.0	37.2	35.5	34.2	
	1.1	21.0	20.9	20.5	17.7	18.8	
Sorghum	2.0	72.7	72.3	70.6	67.7	65.9	
	1.2	43.6	43.4	42.4	40.6	39.5	

The modeling results indicate that atrazine does have the potential to move into surface waters, especially for sugarcane use. Peak EECs for sugarcane, in particular, track very closely with peak levels found in monitoring data in Louisiana streams near sugar cane production areas (See Figure 3 below). Klassen and Kadoum (1979) found atrazine to be persistent in a farm pond ecosystem with estimated half-lives of six to eight months. These data support the persistence of atrazine seen in the gradual reductions in EEC levels produced by the PRZM-EXAMS model presented in the above table. With such stable atrazine concentrations in ponds, only small differences exist between acute and chronic atrazine exposures for ponds. Therefore, the significance of the duration of the toxicity tests conducted becomes less important for assessing risks in ponds.

Data from the EXAMS model were used to estimate the chemical contributions of runoff, erosion and spray drift to the standard farm pond. The results, expressed as percentages, are

tabulated below:

Percent of Pesticide Loadings from Different Sources to the Standard Pond

Use	Runoff	Erosion	Spray Drift
Corn	55.03%	3.47%	41.50%
Sugarcane	99.15%	0.85%	0.01%
Sorghum	71.80%	5.29%	22.91%

The erosion losses were relatively small for all three simulated uses, with runoff and spray drift accounting for most of the loading for corn and sorghum. For sugarcane, most loading in the model simulations was from runoff

Risk Characterization (Pond)

Much of the refined risk assessment that follows is based upon the development of cumulative exceedence curves and comparing them to various horizontal lines representing key effects assessment endpoints. These cumulative exceedence curves are plots of a given type of atrazine exposure concentration against the percentage of the samples, sites, or years with an equal or greater concentrations. They were constructed with Weibull plot positions, which assign a probability to each ranked concentration value as the rank divided by the sum of total number of samples plus one. The intersection of a cumulative exceedence curve with one or more horizontal lines representing key assessment endpoints gives the percentage or percentages of the samples, sites, years with an equal or higher concentration than the assessment endpoint.

The following graphs (Figures 1, 2, and 3) show the PRZM-EXAMS modeled peak, 96-hour, 21-day, 60-day, and 90-day water column dissolved concentrations of atrazine for 36 years (sorghum and corn) and 20 years (sugarcane) and the percentage (%) of years with equal or greater concentrations. Intersecting these curves are horizontal lines representing the key assessment endpoints for ponds found in Table 1. A discussion of the PRZM-EXAMS model and its uncertainties is found in Appendix V.

Considering the exposure values for the 90-day moving average, we estimate that for months every year, modeling simulations indicate that atrazine concentrations in ponds from use on sorghum and sugarcane exceed the levels at which studies have shown reductions in fish and invertebrate populations, macrophytes, and primary production. For corn, modeling simulations indicate that atrazine concentrations in ponds exceed the levels at which studies have shown reductions in fish populations, invertebrate populations, macrophytes, and primary production in 70 to 83% of the years.

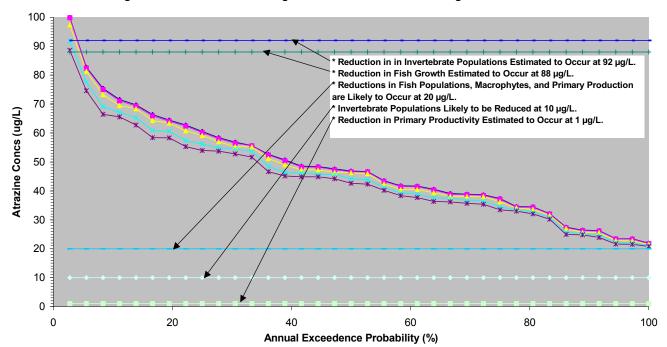
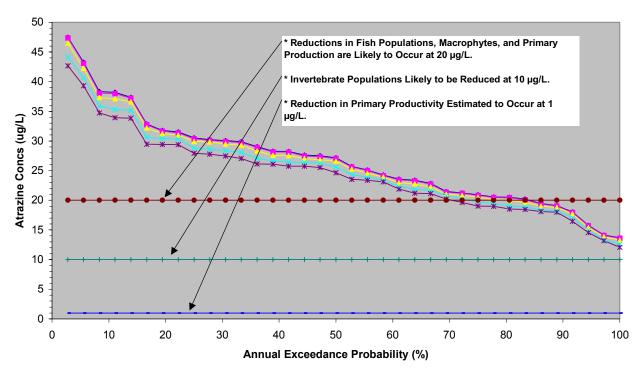


Figure 1. PRZM/EXAMS Modeling Atrazine Results of Kansas Sorghum Pond Scenario

From 70 to 75% of the years, atrazine concentrations in ponds from use on sugarcane exceed the levels at which reproduction studies have shown reductions in invertebrate populations and fish growth. For sorghum, the percentage of exceedences are from 2.8 and <5% of the years, and for corn, there is no year when these two endpoints are exceeded.





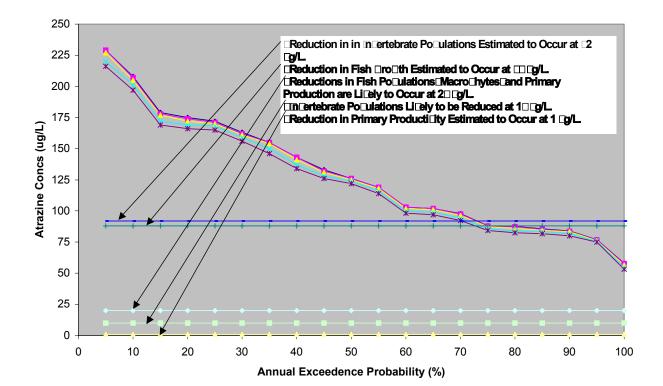


Figure 3. PRZM/EXAMS Modeling Atrazine Results of Louisana Sugarcane Scenario

An Interpretation of the Results

While the standard pond scenario assumes instantaneous mixing, it is more likely that the aquatic vegetation in shallow areas around the edge of the pond, particularly the edge nearest the treated field, as well as in the epilimnion in larger static bodies of water, will be exposed to higher atrazine levels than the mean concentration for the whole pond. The loss of rooted aquatic plants along the edge of a water body has several consequences, including: 1) the release of nutrients into the water which is likely to increase phytoplankton growth, which may decrease light penetration to plants in deeper water. If the plants in deeper water die they too release more nutrients to the phytoplankton. 2) The absence of rooted vegetation along the shore line does not intercept and hold sediments from runoff. Suspension of sediments in the water column adds to the light blockage from phytoplankton. Sediment deposited on plant leaves further reduces the ability of the plant to photosynthesize. One study reported 27 percent reduction in photosynthesis from sediments on the leaves only. (Jones and Estes, 1984) 3) Water movements along the shores from wind-generated waves or other sources may stir up sediments into the water column and onto plant leaves. At some point, the stresses on the ability of plants to photosynthesize from atrazine, sediments and light attenuation exceed the capacity of the plants in deeper water to produce sufficient energy to meet their own needs. The plant dies and repeats

the cycle releasing more nutrients, growing more phytoplankton and causing further attenuation of light, starving more plants in evermore shallow waters.

The loss of the submerged vegetation reduces the availability of habitat for small fish and aquatic invertebrates to avoid predators. With increasing losses of vegetation the populations of aquatic invertebrates and small fish decline as the larger predators consume more prey until the numbers of prey decline. With the loss of the vascular plants, the source of food becomes evermore dependent on phytoplankton to sustain the trophic levels for those animals which survive. For those organisms dependent on vascular plants for food their populations will likely decline as the food sources decline.

Kettle *et al.* (1987) observed the decline in vascular vegetation following a single application of 20 Fg/L to a pond. Within a couple of months the vegetation had declined 60 percent compared to controls. By the following spring, aquatic vegetation was reduced 90 percent. Upon draining the ponds that spring, bluegill young had been reduced 96 percent compared to controls, fish in treated ponds had fewer prey items in their stomachs and some aquatic invertebrate taxa were missing. These indirect community effects on fish and aquatic invertebrate populations are the result of the impact of atrazine on aquatic vegetation.

Exposure Characterization (Lakes and Reservoirs)

Baier *et al.* (1985) reported that in the United States atrazine concentrations may reach up to 88.4 Fg/L in surface water from drinking water reservoirs. Waldron (1974) reported atrazine concentrations up to 69.4 Fg/L from U.S. surface waters.

Atrazine Concentrations in Community Water Supplies (CWSs)

As the tables below show, some high detections (> 20 ug/L) of atrazine have been reported for finished drinking water in the States of Illinois, Indiana, Ohio, and Missouri.

Acetochlor Registration Partnership (ARP) Monitoring Study of Atrazine in Surface Water Source CWSs

214-GI-IL	Gillespie	05/29/96	49.48
214-GI-IL	Gillespie	05/15/96	41.00
219-SH-IL	Shipman	05/29/96	34.65
214-GI-IL	Gillespie	06/12/96	28.68
219-SH-IL	Shipman	05/01/96	25.68
340-NV-IN	North Vernon	05/28/96	24.84
219-SH-IL	Shipman	06/12/96	23.71
330-LO-IN	Logansport	05/27/97	23.11
150-FL-IL	Flora	05/29/96	22.69
455-MO-OH	Monroeville	05/27/97	21.32
219-SH-IL	Shipman	06/27/96	20.61

219-SH-IL	Shipman	07/10/96	20.60
219-SH-IL	Shipman	05/15/96	20.58

Novartis Population Linked Exposure (PLEX) Database of Atrazine Concentrations in CWSs in 21 Sates

1350300-IL		1994	30
	HILLSBORO		
1350150-IL	COFFEEN	1994	30
1350600-IL	SCHRAM CITY	1994	30
1350650-IL	TAYLOR SPRINGS	1994	30
1010225-MO	DREXEL	1994	27
1170400-IL	GILLESPIE	1996	42.00
1170030-IL	KAHO PUBLIC WATER DISTRICT	1996	42.00
1170050-IL	BENLD	1996	42.00
1170250-IL	1170250-IL DORCHESTER		42.00
1170300-IL	EAGERVILLE	1996	42.00
1170650-IL	MOUNT CLARE	1996	42.00
1171200-IL	WILSONVILLE	1996	42.00
1175450-IL	1175450-IL SPRING CREEK WTR ASSN		42.00
0801511-OH	SARDINIA, VILLAGE OF	1996	38.73
3900811-ОН	MONROEVILLE, VILLAGE OF	1997	29.58
4502314-OH	NEWARK, CITY OF	1997	20.75

Risk Characterization - Surface Water Sources for Community Drinking Water

The above data show that a number of finished drinking water sites have atrazine concentrations above levels at which reductions in fish populations, invertebrate populations, macrophytes, and primary production are likely (See Table 2).

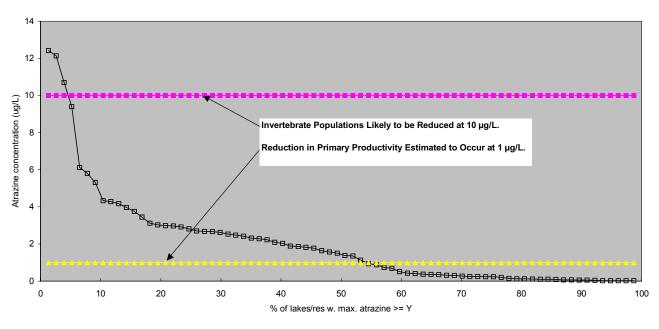
USGS 1992-1993 Study of 76 Mid-Western Reservoirs (USGS Open-File Report 96-393):

The USGS sampled the outflows from 76 midwestern reservoirs 8 times (approximately once every two months) from April 1992 through September 1993 (USGS Open -File Report 96-393). The samples were analyzed for a number of pesticides and pesticide degradates including atrazine, deethyl atrazine (DEA), and deisopropyl atrazine (DIA). The reservoirs were selected from a list of approximately 440 reservoirs in 11 midwestern states.

The sampling frequency was inadequate for EFED to provide atrazine time series (i.e., the fluctuations of concentrations with time) for the reservoirs. However, in Figures 4 and 5, EFED generated 1992 and 1993 cumulative exceedence curves of maximum annual atrazine

concentrations versus the percent of reservoirs with equal or greater annual maximum concentrations. The horizontal line represent the key assessment endpoints found in Table 1.

Figure 4. US□S 1992 Mid-Western La e/Reser oir Sam ling Results
Maximum Atrazine Concentrations



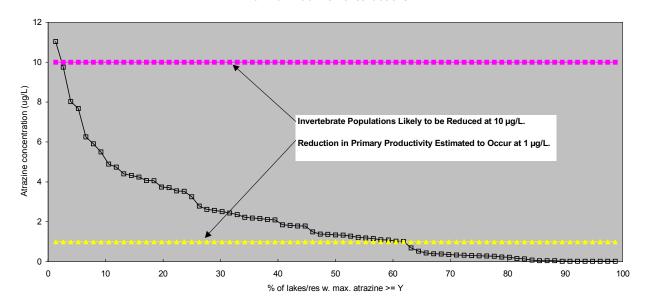


Figure 5. US□S 1993 Mid-Western La □e/Reser □oir Sam □ling Results
Maximum Atrazine Concentrations

Risk Characterization for 76 Mid-Western Reservoirs/Lakes

Based on Figures 4 and 5 for 1992 and 1993, between 55% and 62% of the reservoirs/lakes exceed levels where a reduction in primary productivity is estimated to occur; and, from 2.6% to 5% exceed levels where invertebrate populations are likely to be reduced.

Exposure Characterization (Streams)

Streams receive pulses greater than this level during the primary application period in late spring (Solomon *et al.*, 1996). The highest pesticide concentrations occur in brief pulses following rain events and are usually associated with the storm event soonest after the application. Gilliom *et al.* (1999) have reported that these pulses commonly reach 30 to 40 Fg/L, with a maximum reported value of 108 Fg/L. In some years, atrazine concentrations exceed 100 Fg/L in small (less than fourth-order) streams when storm runoff occurs within a few weeks following planting (Baker *et al.* 1981; Baker 1987). Dilution and degradation usually reduce atrazine concentrations in streams within a few weeks of the rain event (Thurman *et al.* 1992; Moody and Goolsby 1993; Kolpin and Kalkoff 1993). Atrazine concentrations vary from year to year, depending upon usage and rainfall patterns; from watershed to watershed, depending upon the size of the watershed and the intensity of the agricultural activity in it; and within watersheds, depending upon the flow volume and location in the watershed.

Davies *et al.* (1994) reported that atrazine persisted in Tasmanian streams adjacent to treated forested areas for 12 to 16 months following a single application, seepage continued to feed atrazine into streams for months, and they estimated that the half-life in streams is of the order of 3 months.

In 1989/1990 and 1994/95 reconnaissance studies of 50 to 123 midwestern streams, the USGS reported maximum atrazine concentrations during post-application runoff events of 108 ug/L and 50 ug/l, respectively. In a 1995-98 study of 9 Ohio tributaries to Lake Erie, Heidelberg College reported annual maximum atrazine concentrations ranging from 54.6 ug/L to 80 ug/L. Atrazine concentrations in agricultural streams during storm runoff events have been detected at levels as high as 635 Fg/L (M. Langan *et al.*, unpublished; cited by Carder & Hoagland, 1998).

<u>USGS 1989-1990 Reconnaissance Study of Mid-Western Streams (USGS Open-File Report 93-457):</u>

- 1989--one "pre-application" sample, one "post-application" sample and one "Fall" sample from 52, 129, and 143 mid-western streams, respectively, across 10 states.
- 1990--one "pre-application" sample, and one "post-application" sample from 52 and 50 mid-western streams, respectively, across 10 states.
- Samples were analyzed for a number of pesticides including atrazine, DEA, and DIA.
- No time series curves, but cumulative exceedence curves for post-application, and Fall concentrations of atrazine are provided in Figures 6 and 7 to show that atrazine concentrations are highest after the application of atrazine and drop to much lower levels by the fall. The horizontal lines represent the assessment endpoints for streams in Table 2.

120 Reductions in ิ⊓ ertebrate Po ulations Estimated to Occur at 92 g/L for \square 8% of the streams (\square 1). 100 □Reduction in Fish □ rowth Estimated to Occur at 88 □g/L for 1.5% of the streams (□2). ☐Reduction in Macro□hytes Estimated to Occur at 3□ □g/L for 6.2% of the 80 streams (8). Atrazine Concs (ug/L) □īn⊡ertebrate Po⊡ulations Li⊡ely to be Reduced at 22 □g/L for 12.3% of the streams (□ 16). 60 □Reduction in Primary Production Li⊡ely to Occur at 2.62 □g/L for 58% of the streams (□□5). □Reduction in Primary Production Estimated (Lab) to Occur at 1 □g/L for 40 □5% of the streams (□ 9□). 20 10 70 80 20 30 60 90 100 40 50 Exceedence % % Streams w/ Atrazine Concs >= Y

Figure 6. US□S Mid-Western Streams Sam□ling Results for 1989 Post-A□lication Atrazine Concentrations (from 129 Streams)

Risk Characterization for the 1989 Post-Application Stream Monitoring Data

Reductions in invertebrate populations and primary production are likely to occur in 12% to 58% of the Mid-western streams, respectively. In addition, macrophytes are estimated to be reduced in over 6% of the streams. Primary production is also estimated to occur in approximately 755 of the streams.

3.5 3 2.5 Atrazine Concs (ug/L) Reduction in Primary Production Li⊡ely to Occur at 2.62 □g/L for 1.4% of 2 the streams (\square 2). Reduction in Primary Production Estimated (Lab) to Occur at 1 g/L for \square 6% of the streams (\square 11). 1 0.5 0 0 10 20 30 40 70 80 90 100 Exceedence % % Streams w/ Atrazine Concs >= Y

Figure □ US□S Mid-Western Streams Sam□ling Results for 1989 Fall Atrazine Concentrations (from 143 Streams)

<u>USGS 1994-1995 Reconnaissance Study of Mid-Western Streams (USGS Open-File Report 98-181):</u>

- 1994--one "pre-application" sample, and one "post-application" sample from 52 and 50 mid-western streams, respectively, across 8 states (Figure ---).
- 1995--one "post-application" sample from 50 mid-western streams across 7 states.
- Samples analyzed for a number of pesticides including atrazine, DEA, and DIA.
- No atrazine, DEA, and DIA time series curves, but 1994 and 1995 pre-application and post-application cumulative exceedence curves of atrazine, DEA, and DIA;
- Figure 8 shows the 1995 "post-application" cumulative exceedence curve for the stream concentrations in 50 Mid-Western streams. The horizontal lines represent the assessment endpoints for streams in Table 2.

50 * Reduction in Macrophytes Estimated to Occur at 37 μg/L for 9.8% of the sites 45 * Invertebrate Populations Likely to be Reduced at 22 µg/L for 63% of the sites 40 35 Reduction in Primary Production Likely to Occur at 2.62 µg/L for 58% of the sites (~31). Atrazine Concs (ug/L) Reduction in Primary Production Estimated (Lab) to Occur at 1 µg/L for 75% of the sites (~ 38). 20 15 10 5 0 10 20 30 40 50 60 70 80 90 100 Exceedence % % Sites w/ Atrazine Concs >= Y

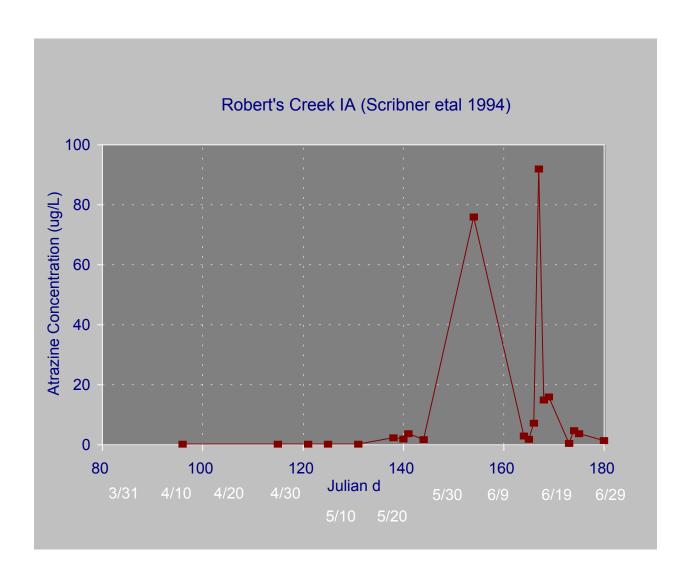
Figure 8. US □ S Mid-Western Stream Sam ling Results for 1995
Post-A □ lication Atrazine Concentrations for 5 □ Streams

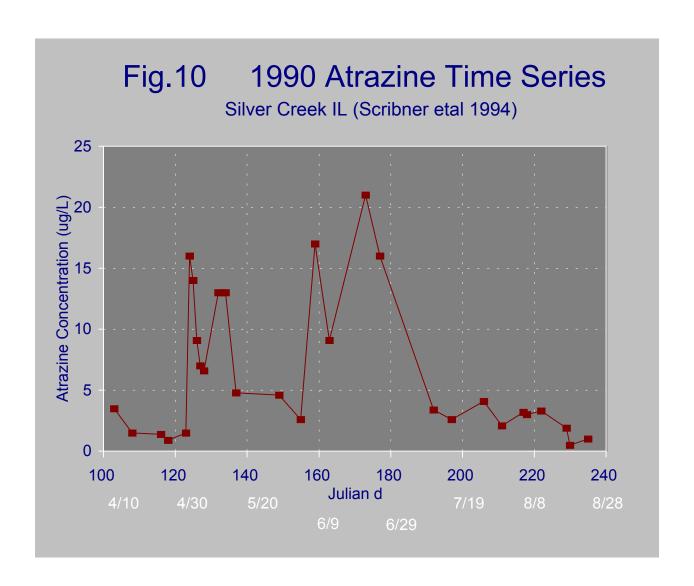
Risk Characterization for the 1995 Post-Application Stream Monitoring Data

Reductions in macrophytes are estimated to occur in almost 10% of the streams, and reductions in invertebrate populations and primary production are likely to occur in 12% to 58% of the Midwestern streams, respectively. In addition, macrophytes are estimated to be reduced in over 6% of the streams. Primary production is also estimated to occur in approximately 75% of the streams.

<u>USGS 1990-1992 Study of 9 Mid-western Rivers/Streams (USGS Open-File Report 94-396):</u>

- Each of 9 mid-western rivers/streams sampled several hundred times from April 1990 through July 1990.
- Samples were collected 1-2 times per week and automatically collected during runoff events either at several hour intervals or in response to changes in flows. During runoff events, 2-4 samples were typically collected at different times on the same day.
- Samples analyzed for a number of pesticides including atrazine.
- No cumulative exceedence curves from the data, but sets of atrazine time series. Multiple samples from a site on the same day are averaged. Two time series graphs are presented in Figures 9 and 10 to show the atrazine concentrations for Robert's Creek Iowa and Silver Creek, Illinois. The maximum concentrations pulse up to 90 Fg/L and regularly exceed 10 Fg/L. The maximum atrazine concentrations for rivers range slightly lower, from 10 to 20 Fg/L.
- These pulse concentrations exceed many of the assessment endpoints in Table 2 for streams. The duration of these high concentrations of atrazine may last for days especially during the spring when numerous fields in a watershed are receiving applications at various times. Thus, it is conceivable that reductions in invertebrate populations and primary production will occur as a result of post-application stream contamination from the spring applications of atrazine.





The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS).

Additional monitoring data on atrazine concentrations for streams are derived from the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS). The NAWQA program is designed to describe the status of and trends in quality of the nation's ground water and surface water resources and to link assessment of status and trends with an understanding of the natural and human factors that affect the quality of water. The building blocks of this program are Study-Unit Investigations in 60 major hydrologic basins of the nation. The 60 NAWQA Study Units cover about one-half of the conterminous United States, and encompass 60 to 70 percent of national water use. The initial results of 20 Study Units are available through the NAWQA web site covering 1991 through 1996. The program is on-going.

The results from "indicator" and "integrator" sites were analyzed for aquatic atrazine exposure data. Indicator sites were chosen to represent water quality conditions of streams in relatively homogeneous basins associated with specific land use and natural characteristics that were targeted for study. In contrast, integrator sites were chosen to represent water quality conditions of streams with relatively large basins that are influenced by complex combinations of land-use settings, point sources, and natural influences typical of the region. Integrator sites generally are downstream from indicator sites and are located at key nodes in the drainage network. Results from the integrator sites provide a general check on the persistence of water quality influences evident at the indicator sites; the results also can be used for water-budget and contaminant transport assessments.

The 65 sites available from the NAWQA web page consist of 40 agricultural indicator sites, 11 urban indicator sites, and 14 integrator sites. In most of the agricultural basins, cropland and orchard-vineyard land account for more than 40 percent of the basin area and urban land accounts for less than 5 percent. Water quality conditions at urban indicator sites are affected primarily by urban, suburban, commercial, and industrial sources. The number of samples are 1606, 650, and 605, respectively, for the 40 agricultural sites, 11 urban indicator sites, and 14 integrator sites. The following 3 figures indicate the distribution of atrazine concentrations found in samples at these 65 sites.

The summaries of concentrations at different percentiles are shown in the following table:

NAWQA DATA Indicator Site (number)	maximum (ug/L)	99 th percentile	95 th percentile	90 th percentile	50 th percentile
agriculture (40)	120.0	13.0	3.25	1.2	0.027
urban (11)	14.0	2.75	0.65	0.33	0.041
integrator (14)	27.0	12.5	5.35	1.95	0.062

Since there were so few integrator and urban sites, EFED focused further analysis on the agricultural sites. The maximum atrazine concentrations were determined for each of the 40 agricultural sites and cumulative exceedence plots based on these maximum site concentrations were graphed and are presented in Figure 11. The horizontal lines represent the key assessment endpoints for streams as listed in Table 2.

130 120 Reductions in in ertebrate Po ulations Estimated to Occur 110 at 92 □g/L for □ 3% of the Sites (□1). Reduction in fish □rowth Estimated to Occur at 88 □g/L for 100 3% of the Sites (□1). Measured Concentations (ug/L) Reduction in Macro□hytes Estimated to Occur at 3□ □g/L 90 for □4.5% of the Sites (□2). 80 □in ertebrate Po ulations Li ely to be Reduced at 22 g/L for 11% of the Sites (□4). 70 Reduction in Primary Production Li⊡ely to Occur at 2.62 60 g/L for 34% of the Sites (□ 14). Reduction in Primary Production Estimated to Occur at 1 50 g/L for □5□% of the Sites (□2□). 40 30 20 10 20 30 40 60 70 80 90 100 10 50 Exceedence % % Sites w/ Atrazine Concs >= Y

Figure 11. National Water Quality Assessment Program (NAWQA): Maximum Atrazine Concentrations for 4□ Agricultural Sites

Risk Characterization for NAWQA Agricultural Sites

Based on monitoring data for these 40 agricultural sites, reductions in invertebrate populations and primary production are likely for from 11% to 34% of the sites. Reductions in fish growth and macrophytes are estimated to occur in 3% to 5% of the sites.

It is important to note that the NAWQA monitoring data were not specifically designed to time monitoring to correspond to atrazine applications or specifically oriented to atrazine treatment areas. Thus, they are likely to underestimate the concentrations likely to be present in streams.

A summary table of population percentiles for the various stream surveys is given below:

USGS (FR93-457)	max val	99 th	95 th	90 th	50 th
(sample number)	(Fg/L)	percentile	percentile	percentile	percentile

Pre-Appl. 1989 (52)	1.7		0.9415	0.666	0.235
Post-Appl. 1989 (129)	108	97.2	43.5	27	4.7
1989 Fall (143)	3.1	2.66	1.28	0.796	0.25
Pre-Appl. 1990 (52)	3.8		1.475	0.866	0.24
Post-Appl. 1990 (50)	33		29.25	25.4	8.1
All Samples (426)	108	50.92	22.65	15	0.465
USGS (F.R.94-396) (sample number)					
All Samples (215)	92	40.84	17	14	2.7
USGS (F.R.93-657) (sample number)					
All Samples (542)	11	8.257	4.685	2.87	0.36
USGS (F.R.98-181) (sample number)					
Pre-Appl. 1994 (53)	2.3		0.355	0.276	0.14
Post-Appl. 1994 (51)	38		25.4	20.8	4.2
Post-Appl. 1995 (50)	50		45.9	35.2	5.55
All Samples (154)	50	48.35	27.25	18.5	1.35

Risk Characterization (Streams in General)

Herbicides may exert an important impact on stream ecosystem productivity and structure. A number of studies have been conducted on the effects of atrazine applications on phytoplankton and a few tests have addressed the more subtle productivity and/or community-level effects. Lakshminarayana $et\ al$. (1992) monitored high atrazine effects on phytoplankton numbers from 9 June to 16 November 1989 at various points on a natural, first-order stream adjacent to a tiled corn field treated with 4 liters per hectare at concentrations of $\leq 1.89\ \text{Fg/L}$ (no replication for statistical analyses). Artificial streams have been used to assess community level effects of atrazine by several authors. Gruessner and Watzin (1996) monitored effects of atrazine concentrations ($\leq 5\ \text{Fg/L}$) typically found in a Vermont stream and found no significant reduction in chlorophyll a levels of attached algae throughout a 14-day exposure, but found a significant increase in the total number of early, aquatic insect emigrants at $\leq 5\ \text{Fg/L}$. Lynch $et\ al$. (1985) also reported a significant increase in insect emergence from streams treated at 25 Fg/L; no significant or lasting effects were found on the structure of macroinvertebrate

populations, periphyton standing biomass or rates of primary production and community respiration, but the results of the study are uncertain, because DMSO was used as the carrier solvent. Carder and Hoagland (1998) found significant ($p \le 0.05$) reductions in benthic mud algae (ranging from 35 to 58% compared to controls) throughout a 4-week, recirculation study at both 15 and 155 ug/L. The lack of atrazine effects at 155 Fg/L on any of the six dominant algal species appeared to be because of their ability to tolerate atrazine commonly encountered in agricultural streams such as Wahoo Creek where they were collected. Krieger et al. (1988) reported significant (p < 0.001) reductions in stream *Aufwuchs* communities exposed to atrazine for 20 days for ash-free dry weight (range 24 to 31% compared to controls) and chlorophyll a levels (30 to 44%) at 24 and 134 Fg/L at 25EC and at 10EC. Only the 134 Fg/L level reduced ash-free dry weight (47%) and in chlorophyll a levels (40%). At 100 Fg/L atrazine (the lowest test concentration), Kosinski and Merle (1984) and Moorehead and Kosinski (1986) reported significantly (p < 0.5) inhibited phytoplankton net community productivity, measured as dissolved oxygen for at least 3 days. While most of the stream studies were on the effects on phytoplankton, the benthic algae account for the bulk of photosynthesis in all but the largest streams (Wetzel, 1975).

Exposure Characterization (Estuaries)

Louisiana

Since 1992 the Louisiana Department of Agriculture and Forestry (LDAF) has collected data on atrazine and other pesticides in surface and ground water. LDAF and the Louisiana Department of Environmental Quality have been collecting surface water data on atrazine in the Upper Terrebonne watershed. Much of the recent Upper Terrebonne data are available on the state internet site at http://www.deq.state.la.us/surveillance/atrazine/index.htm. Data from 1998 are summarized below plotted in Figure 12 as a cumulative exceedence curve with the maximum and mean concentrations by site (28 sites) against the percentage of sites with equal or greater concentrations. The horizontal lines represent the key assessment endpoints for estuarine/marine areas as listed in Table 3.

% prob.	peak	95%	90%	75%	50%
Conc. Max (ppb)	216.2	210.0	125.8	34.7	13.3
Conc. Mean (ppb)	56.7	54.7	24.5	8.0	4.5

225 Considering the Maximum Concentrations: Reduction in ெretebrate Po⊡ulations Estimated to Occur at 123 □g/L for □12% of 200 the Sites (□3). in ertebrtate Mortality Estimated to Occur at 94 □g/L for □16% of the Sites (□5). Marine/Estuarine Algae Mortality Estimated to Occur at 22 □g/L for □35% of the 175 Sites (□1□). Reduction in Macro hytes Estimated to Occur at 1 □ □g/L for □□3% of the Sites (□2□). 150 Atrazine Concs (ug/L) Reduction in Macro hytes Li ely to Occur at 4 g/L for 86% of the Sites (24). Reduction in Primary Production Li⊡ely to Occur at □.12 □g/L for □1 □□% of the Sites (□28). 125 100 75 50 25 0 20 30 70 80 0 10 40 50 60 90 100 Exceedence % % of Sites w/ Atrazine Concs >= Y

Figure 12. Louisiana Max & Mean Atrazine Concentrations By Site (28 Sites) in 1998

Risk Characterization for Louisiana Monitoring Data

Thirty-one stations were sampled either weekly or in conjunction with atrazine "events," i.e., pre-emergent, post emergent, lay-by, or fall applications in areas near bayous, canals and ditches in the Terrebonne watershed. The majority of stations were located downstream on streams that receive runoff from predominantly sugar cane and corn production areas. The data show peak levels over 200 ug/L for more than one station, and over 100 ug/L for at least two more. Although mean levels per station are lower, most are still in a range that could have adverse impact on aquatic life.

At the higher levels from 100-200 ug/L, both invertebrate mortality as well as reduction in invertebrate populations are estimated to occur, these at 12-16% of the sites. Further considering the range of peak concentrations per site, marine/estuarine mortality is estimated to occur for at least one third of the sites, reduction in macrophytes is likely to occur at about 86% of the sites, and reduction in primary production is likely to occur at all sites.

Weekly sampling shows many levels declining substantially from peak within a week's time, but often rising to nearly previous levels the following week. As indicated earlier, the Terrebonne sampling peak levels correspond very closely to peak concentrations predicted by PRZM/EXAMS for ponds in areas of sugar cane production. Predictions and monitored levels further in time (or distance) from the application event, however, begin to diverge for the two types of water bodies.

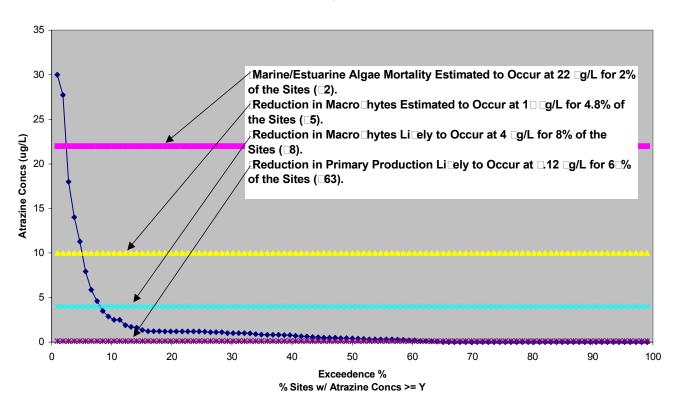
Exposure Characterization for the Chesapeake Estuary

Results from the Chesapeake Bay monitoring data in the following graph (Figure 13) and the summary table below indicate that the maximum atrazine level found was 30 Fg/L and the 95th, 90th, and 75th percentile values are all greater than 1 Fg/L. The data are plotted in Figure 13 as a cumulative exceedence curve with the maximum concentrations by site (40 sites) and year against the percentage of sites with equal or greater concentrations. The horizontal lines represent the key assessment endpoints for estuarine/marine areas as listed in Table 3.

Chesapeake Bay (105 sites)	max conc (Fg/L)	95 th percentile	90 th percentile	75 th percentile	50 th percentile
	30.0	13.5	3.066	1.2	0.415

Figure 13. Surface Water Monitoring Results for Atrazine in the Chesa ea Bay's Tidal Riers

Maximxum Concentrations by Site and Year (19 - 1993)



Risk Characterization for the Chesapeake Bay Monitoring Data

The atrazine concentrations in the Chesapeake Bay are shown to be above levels where primary production and macrophytes are likely to be reduced for 8% to 60% of the sites, respectively. Atrazine could be contributing to reductions in submerged aquatic vegetation and primary productivity at certain sites in the Bay. Additional analyses of the available data are necessary. Specifically, attempts should be made to establish co-occurrence of sites with atrazine concentrations above approximately 4 Fg/L with sites in the bay which are still unable to achieve their submerged aquatic vegetation (SAV) goal.

There are insufficient data to determine definitively that atrazine is a significant contributor to the decline in aquatic vegetation in Chesapeake Bay and other estuaries. It is possible, however, that atrazine and other herbicides used in these watersheds are a source of stress to aquatic vegetation. Another important stressor is eroding sediment from development in the watershed and this, combined with herbicide residues, could negatively affect estuarine ecosystems.

The Chesapeake Bay is an example of an estuary that could be affected by atrazine use. The Chesapeake is important ecologically and economically. The upstream section of most rivers feeding the Chesapeake is generally freshwater while downstream, nearer the Bay, the waters are brackish and tidal. Corn is a major crop in the Chesapeake watershed, and atrazine is an important herbicide. Atrazine could impact other estuarine areas where corn or sugarcane are grown.

Atrazine has been detected in ground and/or surface waters of the Chesapeake Bay watershed (Stevenson *et al.*, 1978, Wu, 1980; Kemp *et al.*, 1982; Glotfelty *et al.*, 1984; Hall and Anderson, 1991). Herbicides, including atrazine, represent a potential source of stress for estuarine vegetation and have been suggested as a possible cause for the decline of submerged aquatic vegetation in Chesapeake Bay (Correll *et al.* 1978).

Numerous species of submerged vascular plants were important in this estuarine ecosystem until about the mid-1970's when their abundance declined (Bayley *et al.*, 1978; Stevenson and Confer, 1978; Orth and Moore, 1983, 1984; Orth *et al.*, 1991). Prior to the decline of the submerged aquatic vegetation (SAV) in the Chesapeake in the 1970's, these plants were responsible for 40% of the relative primary production in the Chesapeake. After the decline, SAV produced less than 10 % of the primary production (Anderson, 1981). According to surveys by the U.S. Fish and Wildlife Service, 28% of their Chesapeake Bay stations were vegetated in 1971 compared to about 10% of the stations in 1978. Although SAV reductions could be identified in several distinct areas of the Chesapeake, the overall decline appears to have been random (Cohen, 1985).

The decline in estuarine vegetation stimulated atrazine research on a number of vascular plants. Atrazine concentrations as low as 4 to 10 Fg/L have been shown to reduce plant growth and productivity in 5 SAV species after exposures of 5 or more weeks (Forney and Davis, 1981; Jones and Winchell, 1984; Cohen, 1985; Jones *et al.*, 1986). Atrazine levels of 50 to 150 Fg/L inhibit photosynthesis by 50% for various SAV species (Forney & Davis, 1981; Correll and Wu, 1982; Jones *et al.*, 1982; Kemp *et al.*, 1982; Cunningham *et al.*, 1984; Delistraty and Hershner, 1984; Jones and Estes, 1984; Jones and Winchell, 1984; Jones *et al.*, 1986). One to two-hour atrazine exposures resulted in the 50% reductions in photosynthesis in some of the above studies. Jones *et al.* (1986) showed that the uptake of atrazine by vascular aquatic plants occurred within 15 minutes. Plants appeared to recover after 2-hour washing with atrazine-free water, although some indications of depression of photosynthesis remained at the end of the 77-hour recovery period.

Jones and Estes (1984) studied different routes of atrazine toxicity based on measurements of the photosynthetic response of pondweed, *Potamogeton perfoliatus*, to atrazine in water (0 and 100 Fg/L) and in sediment on the leaves (0 and 120 Fg/kg) and found 27 percent reduction from shading with sediment, 8% reduction attributable to atrazine in sediment on leaves, and 69% from atrazine in water and no sediments. The range of photosynthetic effects were from 69% for water alone to 83% for water and atrazine-free sediment on leaves. These results show that sediment shading alone reduces photosynthesis by up to 27%, that atrazine in sediments has little added effect, and the major source of toxicity is from water exposure. One-week exposures to 1

Fg/L atrazine reduced chlorophyll production (41 to 93%) in 5 estuarine phytoplankton.

Atrazine concentrations in the upper reaches of shallow estuarine creeks adjacent to atrazine-treated corn are expected to yield the highest atrazine concentrations in the Chesapeake Bay. Atrazine levels in the upper parts of tidal creeks may persist for days as the atrazine-laden water moves back and forth in the creek with daily tidal flow. In areas like these creeks, Kemp *et al.* (1982) found concentrations as high as 100 Fg/L in shallow water close to agricultural fields, which are at least 3 times the highest level cited in the above monitoring data.

Toxicity of Degradates Compared to Parent Atrazine

Atrazine degradates were considered with respect to prolonged toxic effects following atrazine degradation. Listed in the table below are the available toxicity values used for a comparison of atrazine and its four primary degradates.

	Toxicity Co	omparison of A	trazine with it	ts Degradates	
Test Type	Atrazine	Hydroxyatrazine	Deethylatrazine	Deisopropylatrazine	Diaminochloroatrazine
Mammalian Acute Oral LD ₅₀ (mg/kg)	97 % ai	97.1 % ai	95.7% ai	96.7 % ai	98.2 % ai
Female Male	1,190 ² 1,317 ²		668 (1.78) ³ 1,891 (0.70)	810 (1.47) 2,290 (0.58)	
Male & Female	1,869²		1,111 (1.1)	1,240 (1.01)	
Combined Oral LD ₅₀ Male & Female	1,8694		1,111 (1.7)	1, 240 (1.5)	
Mammalian Gestation (Days 6-15) ppm	200 / 1,4005	500 / 2,500 (0.4)	25 / 100 (10)	5 / 25 (40)	50 / 500 (4.0)
Carcinogenicity 2-Year	10 / 70	10 / 25			
Carcinogenicity 2-Year	70 / 400	25 / 200			
Algae (Cell counts) 12-14-day EC ₅₀ :					
Anabaena inaequalis	30	> 10,000 (< 0.003)	1,000 (0.03)	2,500 (0.012)	7,000 (0.004)
Scenedesmus quadricauda	100	> 10,000 (< 0.01)	1,200 (0.08)	6,900 (0.01)	4,600 (0.02)

²Atrazine purity 85.5 %ai

³Atrazine/degradate toxicity ratio

⁴Most toxic atrazine technical value

⁵NOAEC / LOAEC values, NOAEC values were used to estimate toxicity ratios

Chlorella pyrenoidosa	300	> 10,000 (< 0.03)	3,200 (0.09)	> 10,000 (< 0.03)	> 10,000 (< 0.03)
Anabaena variabilis	4,000	> 10,000 (< 0.4)	3,500 (1.1)	5,000 (0.8)	> 10,000 (< 0.4)
Anabaena cyclindrica	1,200	> 10,000 (< 0.12)	8,500 (0.14)	> 10,000 (< 0.12)	> 10,000 (< 0.12)

The major atrazine degradates are generally long-lived and appears to be about toxicologically equivalent to atrazine for mammals, but much less toxic to algae than atrazine. Toxicity data for these degradates are unavailable for birds, fish, aquatic invertebrates, terrestrial plants, and acute oral mammals for comparison.

The dealkylatrazine degradates are more acutely to female rats and more chronically toxic to gestating rat pups than the parent atrazine (ratios greater than 1). The acute comparison was made using an atrazine 85.5% WP formulation, the most toxic atrazine form with both male and female toxicity values. Toxicity data for male and female acute toxicity values were not available for technical grade atrazine data. Combined male and female acute toxicity values for dealkalatrazine degradates were similar to the most acutely toxic technical grade atrazine value (i.e., ratios 1.1 and 1.01). The dealkylatrazine degradates were also more toxic to rat pups during gestation than the parent atrazine. However, the dealkylatrazine degradates were generally less toxic (ratios less than 1) to algae than atrazine. Toxicity data are unavailable for birds, fish, aquatic invertebrates and terrestrial plants for comparison. Based on the available degradate toxicity data, all of the atrazine degradates are appear to be more acutely and chronically toxic to mammals than the parent atrazine, except for algae. Hence, the acute and chronic risks to mammals would persist longer than risks from the parent atrazine.

Incidents

The Ecological Incident Information System (EIIS) maintained by EFED has a total of 109 reported incidents from 1991 through 1999. Thirteen incidents are classified as "Unlikely", 50 are listed as "possible" and two are "Unrelated;" with one exception, they are not discussed further. In only one case, a 1996 cotton use in Louisiana, was casualities (fish carcasses) analyzed for atrazine residues. Shad and carp tested positive for atrazine, but the conclusion was that atrazine was unlikely the cause of mortalities (I004021-004).

Forty incidents are considered "Probable," and four incidents are listed as "Highly Probable." The 4 incidents listed as "Highly Probable" include 3 home/lawn use incidents and 1 corn use incident. The corn use incident reported affecting 100 bass and 100 bream (# B000163-001) resulting from registered use. The three home/lawn incidents were lawn applications which affected grass; two were concluded to be misuse/accidental (# I005579-001, I005132-001). The third home incident (# I001910) was a registered EC use which affected grass and non-target plants.

The forty "Probable" incidents include: 16 (40 %) cases affecting corn; 11 (27.5 %) affecting grass; 11 (27.5 %) fish kills; 1 bird kill case; and affects on ornamentals (2 cases), fruit trees (2 cases), berries (1), garden (1), oats (1), runoff killed vegetation around an atrazine/cyanazine-treated field and pond irrigation water killed greenhouse plants. Four "probable" incidents are classified as misuse (accidents): two cases from corn use (I005879-003, pears, raspberry and oats and I007371-013, grass and ornamentals); and two lawn misuse cases: I009445-031, grass; and I009445-029, bluegrass.

Analysis of 14 corn incidents occurring in 1999 which were submitted by Novartis indicates that in all cases, formulations of Bicep II (a mixture of atrazine and metolachlor) were used. The reported applications rates ranged from 1.4 quarts of atrazine /1.4 quarts of metolachlor to 2.6/2.6 quarts/A. Effects included distorted and cupping leaves, failure to unfurl, uneven height, chlorotic yellowing and necrotic leaves, and killed. Corn acreage affected ranged from 55 to 55 percent of 600 acres.

There were 11 grass incidents resulting from home/lawn uses; three of these cases are considered to misuse (accidental).

Given the low toxicity of atrazine to fish, the reason for the frequency of fish kill incidents is uncertain. About 60 percent of the reported fish kills listed under atrazine in the incident record occur during the Spring when atrazine is applied, soils are saturated and heavy rainfall is frequent. Heavy runoff may carry atrazine, other pesticides and organic loads into surface waters. The high volume and wide-spread use of atrazine increases the probability of co-occurrence of fish kills with atrazine applications. There are some other scenarios which may explain atrazine induced fish kills as well as causes unrelated to atrazine use.

Three plausible scenarios could exist in which atrazine applications may be responsible for the fish kills. First, atrazine concentrations in surface waters from runoff and/or spray drift may be much higher in shallow water adjacent to treated fields than estimated by EFED or found in monitoring studies. Second, atrazine in surface water may kill aquatic plants and the decaying process of dead plants may lower dissolved oxygen to levels too low for fish survival. Third, atrazine is known to increase the toxicity of organophosphate insecticides, such as chlorpyrifos, and a number of other pesticides which may have been applied earlier to atrazine-treated crops or applied in other fields upstream in the watershed.

Possibilities also exist that other causes, not atrazine, may be responsible for some or all of the reported atrazine incidents. Heavy organic loads consume oxygen from the water as the organic matter oxidizes, thereby causing low dissolved oxygen levels which may cause fish to suffocate and die. Other pesticides in the watershed killed the fish as the water flowed past atrazine-treated fields. Since limited information is available in the atrazine incident records, such as water and tissue analyses, conclusions of responsibility would appear to be uncertain and the result of coincidence with little evidence for cause and effect.

Certainty / Uncertainty

In spite of the uncertainties listed below, it is very important to note that the atrazine monitoring data are very robust and enable a refinement of the ecological risk assessment. It is also important to note that this large body of surface water monitoring data, combined with extensive effects data for aquatic organisms, enables EFED to draw conclusions for atrazine with greater certainty than for virtually any other herbicide.

This refined assessment, while providing a greater certainty of adverse effects on aquatic life than that based on modeled exposure and typical laboratory toxicity values, also contains inherent uncertainties. Two important sources of uncertainty can be attributed to the monitoring data and the laboratory and field study data themselves. The monitoring data were not collected for the purpose of supporting an environmental risk assessment. Thus, the spatial and temporal distributions of the monitoring data do not match those for the laboratory toxicity studies or the field studies. Another important uncertainty with regard to using monitoring data for the atrazine ecological risk assessment is that there are little or no monitoring data for some areas that might be most vulnerable. These include prairie potholes, first-order streams, wetlands, ponds, and playa lakes near high-use areas where community-level impacts could be locally significant.

Much of the monitoring data used to assess risks to aquatic organisms in streams and rivers and the Chesapeake Bay can not be interpreted to be the worst case scenario. The data are generally from random sampling sites in a watershed. There is no indication that the samples were collected from areas near atrazine-treated fields or that the samples were collected during the periods of application and the first heavy runoff after application. Also most of the sampling was not on a frequent enough basis to determine the duration of atrazine exposures in flowing water. Rather, these monitoring data present a random snapshot of what atrazine levels are present in a number of watersheds.

The laboratory and field study data for the most part are taken from published literature. The EPA scientists did not have access to the raw data necessary to evaluate some of these studies as is typically done for data submitted by registrants to support registration. Also, while a majority of the laboratory and field toxicity data indicated similar effects at similar exposure levels, there were a few studies that showed no effects at similar exposure levels. In addition, while the laboratory toxicity data indicate adverse effects to certain classes/class of organisms, we cannot determine with certainty that there is a commensurate loss of ecological function in natural systems. However, these data do allow us to comment on the loss of diversity in some systems.

IV. Environmental Fate Assessment

Atrazine can contaminate nearby non-target plants, soil and surface water via spray drift during application. Atrazine is applied directly to target plants during foliar application, but pre-plant and pre-emergent applications are generally far more prevalent.

The resistence of atrazine to abiotic hydrolysis (stable at pHs 5, 7, and 9) and to direct aqueous photolysis (stable under sunlight at pH 7), and its only moderate susceptibility to degradation in soil (aerobic laboratory half-lives of 3-4 months) indicate that atrazine is unlikely to undergo

rapid degradation on foliage. Likewise, a relatively low Henry's Law constant (2.6 X 10⁻⁹ atm@n³/mol) indicates that atrazine will probably not undergo rapid volatilization from foliage. However, its relatively low octanol/water partition coefficient (Log $K_{ow} = 2.7$), and its relatively low soil/water partitioning (Freundlich K_{ads} values ≤ 3 and often ≤ 1) may somewhat offset the low Henry's Law constant value thereby possibly resulting in some volatilization from foliage. In addition, its relatively low adsorption characteristics indicate that atrazine may undergo substantial washoff from foliage. It should also be noted that foliar dissipation rates for numerous pesticides have generally been somewhat greater than otherwise indicated by their physical chemical and other fate properties. In terrestrial field dissipation studies performed in Georgia, California, and Minnesota, atrazine dissipated with half lives of 13, 58, and 261 days, respectively. The inconsistency in these reported half-lives could be attributed to the temperature variation between the studies in which atrazine was seen to be more persistent in colder climate. Long term field dissipation studies also indicated that atrazine could persist over a year in such climatic conditions. Although persistent, atrazine did not seem to leach into lower soil depths. A foresty field dissipation study in Oregon (aerial application of 4 lb ai/A) estimated an 87 day half-life for atrazine on exposed soil, a 13 day half-life in foliage, and a 66 day halflife on leaf litter.

Atrazine is applied directly to soil during pre-planting and/or pre-emergence applications. Atrazine is transported indirectly to soil due to incomplete interception during foliar application, and due to washoff subsequent to foliar application. The available laboratory and field data are reported above. For aquatic environments reported half-lives were much longer. In an anaerobic aquatic study, atrazine overall, water, and sediment half-lives were given as 608, 578, and 330 days, respectively.

Deethyl-atrazine (DEA; G-30033) and deisopropyl-atrazine (DIA; G-28279) were detected in all studies (Appendix II), and hydroxy-atrazine (HA; G-34048) and diaminochloro-atrazine (DACT; G-28273) were detected in all but one of the listed studies. Deethylhydoxy-atrazine (DEHA; GS-17794) and deisopropylhydroxy-atrazine (DIHA; GS-17792) were also detected in one of the aerobic studies. All of the chloro-triazine and hydroxy-triazine degradates detected in the laboratory metabolism studies were present at much less than the 10% of applied that the EFED uses to classify degradates as "major degradates".

For studies limited to several months, the relative concentrations of the degradates in soil were generally DEA>DIA>DACT~HA. However, for an aerobic soil metabolism study and an anaerobic aquatic metabolism study both lasting a year, the concentration of HA was comparable to that of DEA over the last few months of the studies. In addition, some literature indicates that higher quantities of HA can be formed in soil and in sediment under acidic conditions. Other hydroxy-triazine degradates have only rarely been detected in lab studies.

The structures of atrazine, DEA, DIA, DACT, HA, DEHA, DIHA, and diaminohydroxy-atrazine (DAHA) are provided in Appendix I. Note that DIA and DACT are also degradates of simazine. In addition, DACT is also a degradate of cyanazine.

The soil/water partitioning of atrazine, DEA, DIA, and DACT are relatively low as shown by Freundlich adsorption coefficients of < 3 and often < 1 for 4 different soils. The Freundlich adsorption constants for HA are substantially greater, being approximately 2 for sand, but 6.5, 12.1, and 390 for a sandy loam, loam, and clay soil, respectively. No adsorption/desorption data are available for other hydroxy-triazine degradates. However, the higher soil/water partitioning exhibited by HA compared to atrazine suggests that the other hydroxy-triazines are likely to exhibit higher soil/water partitioning than corresponding chloro-triazine degradates.

In a limited study on atrazine and its chloro-degradates in surface water source CWSs, the detection of all was relatively widespread. However, atrazine predominated with the relative order of concentrations generally being atrazine >>DEA>DIA~DACT.

In the Novartis Rural Well Survey (Tierney, et al., 1999), which also included four hydroxy-triazine degradates as analytes, the four hydroxy-triazine degradates were all detected. Of the hydroxy-triazine degradates, hydroxy-atrazine was detected the most frequently and generally at the highest level, but not to the same extent as atrazine or the chloro-triazine degradates. The percentages of detection above a LOD of 0.1 ug/L in the Rural Well Survey for atrazine, DEA, DIA, DACT, HA, DEHA, DIHA, and DAHA were 26.8%, 32.0%, 16.7%, 25.9%, 6.11%, 2.99%, 0.27%, and 0.33%, respectively. Unlike in the surface water study on degradates where atrazine concentrations were generally much greater than chloro-triazine degradate concentrations, the DEA, and DACT chloro-triazine degradate concentrations in the Rural Well Survey were often comparable to those of atrazine. The relative order of concentrations in the Rural Well Survey was generally atrazine~DEA~DACT>DIA>HA.

The relatively widespread detection of atrazine and various chloro-triazine degradates in the surface water study on degradates and in the Rural Well Survey is consistent with the widespread use of atrazine, the persistence of atrazine and the mobility of atrazine and its chloro-triazine degradates. The lower frequency of detection and generally lower levels of the HA in the Rural Well Survey is consistent with its higher soil/water partitioning than atrazine and the chloro-triazine degradates.

The available fate and ground water data indicate that hydoxy-triazine degradates other than possibly HA are unlikely to significantly contaminate surface water. They are not appreciably formed in soil, and they are likely to exhibit higher soil/water partitioning than corresponding chloro-triazine degradates. In addition, they were detected much less frequently and at much lower levels than hydroxy-atrazine in the Rural Well Survey.

The substantially higher soil/water partitioning and generally slower rate of formation in soil exhibited by HA compared to atrazine and some of the chloro-triazine degradates indicate that it is likely to have a lower potential for surface water contamination. However, HA was detected in 6.1% of the samples in the Rural Well Survey at concentrations up to 6.5 ug/L. Also, there have been reported concentrations of HA in soil sometimes approaching and possibly in some cases (e.g., acidic soils) exceeding that of DEA. Therefore, occasional significant contamination of surface water by HA cannot be ruled out by the EFED without at least some screening data.

Atrazine should be somewhat persistent in ground water and in surface waters with relatively long hydrologic residence times (such as in some reservoirs) where advective transport is limited. The reasons for this are the resistence of atrazine to abiotic hydrolysis and to direct aqueous photolysis, its only moderate susceptibility to biodegradation, and its limited volatilization potential as indicated by a relatively low Henry's Law constant. As will be discussed later, atrazine has been observed to remain at elevated concentrations longer in some reservoirs than in flowing surface water or in other reservoirs with presumably much shorter hydrologic residence times in which advective transport greatly limits its persistence.

The relatively low soil/water partitioning of atrazine and chloro-triazine degradates indicates that their concentrations in/on suspended and bottom sediment in equilibrium with the water column will be somewhat comparable. However, despite relatively low soil/water partitioning, limited data indicated that activated carbon can be effective in reducing atrazine and its triazine degradate concentrations by several fold to over an order of magnitude depending upon the frequency and conditions of its use.

Atrazine has been widely detected in rainfall. A USGS study (reference 16) showed that the highest concentrations of atrazine occur in the high use, midwestern corn belt during the application season (mid-April through mid- July). Volume-weighted concentrations ranging from 0.2 to 0.9 µgL⁻¹ were reported in the late spring and summer of 1990 and 1991. In addition, the chloro-degradates DEA and DIA were also detected in rainfall together with atrazine. Moreover, high ratios of DEA to atrazine (approximately 0.5) were attributed to atmospheric degradation. Mass deposition of atrazine and degradates have been found to be higher in the midwestern corn belt, but to decrease with distance away from the corn belt. The USGS study estimated that approximately 0.6% of applied atrazine was annually deposited in rainfall over the study area.

V. Drinking Water Assessment

A separate document titled *Drinking Water Exposure Assessment for Atrazine and Various Chloro-triazine and Hydroxy-triazine Degradates* is attached as a separate document. The following is the Executive Summary taken from the drinking water assessment.

EXECUTIVE SUMMARY

The Office of Pesticide Programs' Environmental Fate and Effects Division (EFED) has analyzed the data from four major surveys of surface and ground water to assess the contribution of atrazine and its major chloro- and hydroxy- degradates to drinking water. This drinking water exposure assessment will be used by OPP's Health Effects Division (HED) in its dietary risk assessment for atrazine.

Results from the largest database indicate an overall level of approximately 10% detection of atrazine residues in samples and community water systems (CWSs) in states with major atrazine

use. The occurrence of atrazine in these surface water sourced CWSs appears to be much more common than in ground water sourced CWSs (37.2% compared with 3.5%). In a survey of targeted rural wells, however, the occurrence was much higher, close to 24% detection for atrazine and 34% for atrazine or its chloro- degradates.

Data from these surveys do not indicate short-term exposure exceedences for atrazine and its degradates when compared to EPA Health Advisory Levels (HALs) or Drinking Water Levels of Comparison (DWLOCs) provided by HED for acute effects. A number of systems were identified, however, where sustained levels of total chloro-triazines were at or above HED's levels of concern for chronic and subchronic effects. Some data were presented on the effectiveness of water treatment for atrazine, and it was shown that a number of systems were able to reduce their average levels with activated carbon.

Sources of Data Analyzed

The exposure assessment of atrazine in Community Water Supplies (CWSs) is based primarily on an analysis of the Novartis Population Linked Exposure (PLEX) database (Section 4). The database includes atrazine concentrations in thousands of CWSs in 21 major atrazine use states over the 1993-1998 period, and also includes the populations served by the CWSs. The CWSs with data in the PLEX database include those with ground water, surface water, and combination (blend) of ground and surface water sources. The data were collected quarterly by CWSs to comply with the monitoring requirements of the Safe Drinking Water Act (SDWA).

The exposure assessment of atrazine and its chloro- and hydroxy-triazine degradates in non-CWS rural well ground water is based upon an analysis of results from the Novartis/States Rural Well Survey (Section 5) and data on atrazine concentrations in 177 wells from the Acetochlor Registration Partnership (ARP) Monitoring Study (reference 10; see Section 8).

In addition, data on atrazine concentrations in surface water sourced CWSs from the Novartis Voluntary Monitoring Study (VMS) and the ARP Surface Water Monitoring Study were statistically analyzed (See Sections 6 and 7, respectively). Those studies on surface water sourced CWSs include fewer than 100 CWSs and 175 CWSs, respectively, compared with the thousands of CWSs included in the PLEX database. However, because samples were taken more frequently than for the PLEX database, the VMS and ARP studies provide far more time series data per CWS than the Novartis PLEX database which has just one data point per quarter per CWS.

Additional data on atrazine concentrations in OH CWSs (reference 13), in IL CWSs (reference 14), in TX CWSs (reference 15), and in CWSs in several states (reference 16) are also briefly discussed (see Section 9).

Estimating Concentrations of Chloro-triazine Degradates

Limited data on the concentrations of chloro-triazine degradates in surface water sourced CWSs

(reference 11) were used to develop regression equations relating the sum of chloro-triazine degradate (DEA, DIA, and DACT) concentrations to atrazine concentrations (see Section 3.1). The regression equations were applied to other PLEX, VMS, and ARP data on atrazine concentrations in surface water sourced CWSs to estimate the sum of atrazine and its major chloro-triazine degradate concentrations (see Section 3.1).

General Results

Because the chloro-triazine degradates are judged to be of toxicological concern, results are presented for both parent atrazine and for total chloro-triazines (TCT) in ground or surface water sourced finished drinking water. General findings are as follows:

Of the 21,241 CWSs in 21 states with atrazine data in the CWS PLEX database through 1998, 2,386 CWSs (11.2%) had one or more atrazine detections above limits of quantification (LOQs). Of a total of 88,766 samples in the database, 8,685 (9.8%) had detections above the LOQs. The LOQs varied from 0.01 to 0.5 ug/L, but were typically at 0.1 ug/L. These data apply to the CWSs in the PLEX database for states in the Atrazine Use Area.

Individual Values and Acute Levels of Concern

No systems exceeded HED's drinking water level of comparison (DWLOC) for acute effects of 298 parts per billion (ppb) for the five-year period (1993-1998) of quarterly monitoring in the PLEX database. The peak total chloro-triazine (TCT) level for any system was 60 ug/L, while the highest individual level of parent atrazine in PLEX during the five-year period was 42 ug/L. Levels of parent atrazine did not exceed the Office of Water's Health Advisory Level (HAL) of 100 ug/L, either.

For the subsample of systems included in the Voluntary Monitoring Study (VMS), the Acetochlor Registration Partnership (ARP) Study, and the Rural Well Survey (RWS), concentrations were sometimes higher than those in the PLEX database, but again no systems exceeded the HED acute DWLOC and only one system exceeded the OW HAL. Individual peak TCT levels ranged from 18 ug/L in shallow ground water (RWS) to 89 ug/L in surface water systems (VMS). Maximum levels of parent atrazine ranged generally from 12 ug/L (RWS) to 64 ug/L (VMS), although one sample in the ARP Ground Water study had a concentration of 132 ug/L atrazine.

Annual and Seasonal Means and Chronic/Subchronic Levels of Concern

For annual and quarterly mean concentrations that represent longer-term exposure, a number of systems serving a substantial number of people had sustained levels of the analytes at or above levels of concern for chronic and subchronic effects. Quarterly mean TCT levels were as high as 42-62 ug/L in systems sampled in the VMS, with as many as six systems in one year exceeding the chronic/subchronic DWLOC of 18 ug/L for 11,458 people. Data from the ARP showed quarterly mean levels as high as 34 ug/L, with three systems' quarterly means >18 ug/L in 1996,

serving 15,865 people in the survey.

Annual mean TCT values ranged as high as 24 ug/L (ARP) and 25 ug/L (VMS), with one or two systems in a given year exceeding the chronic/subchronic DWLOC for the year. Data from VMS show that for 1994, 8,060 people were served by systems in the survey having an annual average TCT concentration of over 18 ug/L. One system in the ARP serving an estimated 365 people had an annual mean >18 ug/L during the 1995-97 period.

EFED also noted systems from the PLEX database whose TCT levels approached or exceeded 18 ug/L. Because only one sample per quarter was analyzed for each CWS in PLEX, that sample may underestimate the quarterly mean for the system or may overestimate it. The drinking water assessment performed by HED will employ a probabilistic approach that goes beyond individual comparisons with a pre-determined level.

For the parent chemical, the maximum annual mean atrazine concentration for individual years from 1993 to 1998 ranged from 4.30 ug/L to 12.0 ug/L in the PLEX database. Of the 21,241 CWSs with atrazine data in the database, 182 CWSs had one or more annual mean parent atrazine concentrations ≥ the MCL of 3 ug/L during the 1993-1998 period. Most of these were in the 3-6 ug/L range.

Of the 182 CWSs mentioned above for potential "multiple exceedence," 81 were actual independent suppliers. Of these, 33 are in Illinois, 16 are in Missouri, 12 are in Kansas, 12 are in Ohio, 4 are in Kentucky, 2 are in Indiana, and one each are in North Carolina and Texas.

Water Treatment Effects

There were limited data from which to determine whether treatment was effective in removing atrazine residues from drinking water. However, such a comparison was possible for part of the VMS data. A comparison of a limited number of raw and treated samples from the VMS indicated that of the 15 CWSs having one or more finished atrazine annual means \geq 3 ug/L, 10 of these systems would have had one or more additional finished annual means \geq 3 ug/L without activated carbon treatment.

Time series are also provided in the Appendix B-4 for 15 CWSs which (based upon raw water data) would have had one or more annual means \geq 3 ug/L without activated carbon treatment. As before, the substantial (several fold) reduction in atrazine concentrations in those systems with the use of activated carbon treatment can be seen from a comparison of the raw and finished water time series for each CWS.

Other studies examined by EFED have looked at the effectiveness of a variety of treatment processes on the removal of various chemicals from the drinking water of systems of different sizes, types and locations. Powdered activated carbon treatment has been shown to remove 28-87% of atrazine residues from raw water. In addition, reverse osmosis methods have demonstrated significant reduction in triazine levels where employed under certain

circumstances (reference 17). EFED is in the process of a continuing evaluation of current methodology available for these and other pesticides.

VI. Environmental Risk Assessment

The fate, drinking water, and ecological effects assessments are found in the appendices. The risk assessment is presented with the fate characteristics for both maximum and typical application rates for the major uses (i.e., corn, sorghum, and sugarcane) and some select minor uses.

A. Summary of Risk Assumptions

The basic process used by EFED integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of integrating the results of exposure and ecotoxicity data is called the quotient method. For this method, risk quotients (RQs) are calculated by dividing exposure estimates by ecotoxicity values, both acute and chronic.

RQ = EXPOSURE/TOXICITY

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are criteria used by OPP to indicate potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) acute - potential for acute risk and regulatory action may be warranted in addition to restricted use classification (2) acute restricted use - the potential for acute risk exists, but may be mitigated through restricted use classification (3) acute endangered species - the potential for acute risk to endangered species exists and regulatory action may be warranted, and (4) chronic risk - the potential for chronic risk exists and regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to nontarget insects, or chronic risk from granular/bait formulations to mammalian or avian species.

The ecotoxicity test values (i.e., measurement endpoints) used in the acute and chronic risk quotients are derived from the results of required studies. Examples of ecotoxicity values derived from the results of short-term laboratory studies that assess acute effects are: (1) LC50 (fish and birds) (2) LD50 (birds and mammals (3) EC50 and EC05 or NOEC (aquatic plants and aquatic invertebrates) and (4) EC25 and EC05 or NOEC (terrestrial plants). Toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are NOAEL and LOAEL for birds and mammals and NOAEC and LOAEC for fish and aquatic invertebrates. The NOAEL or NOAEC values are used as the ecotoxicity test value in assessing chronic effects.

There is a large body of atrazine toxicity data on aquatic plants that assess many different

endpoints (e.g., O_2 production, nutrient uptake, chlorophyll and carotenoid levels, and growth). However, to be consistent with other risk assessments, only the standard registrant-submitted data are used to calculate risk quotients.

Risk presumptions, along with the corresponding RQs and LOCs are tabulated below.

Risk Presumptions for Terrestrial Animals

Risk Presumption	RQ	LOC
Birds and Mammals		
Acute High Risk	EEC¹/LC50 or LD50/sqft² or LD50/day³	0.5
Acute Restricted Use	EEC/LC50 or LD50/sqft or LD50/day (or LD50 < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC50 or LD50/sqft or LD50/day	0.1
Chronic Risk	EEC/NOAEC	1

¹ abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items

Risk Presumptions for Aquatic Animals

Risk Presumption	RQ	LOC
Acute High Risk	EEC¹/LC50 or EC50	0.5
Acute Restricted Use	EEC/LC50 or EC50	0.1
Acute Endangered Species	EEC/LC50 or EC50	0.05
Chronic Risk	EEC/NOAEL	1

 $^{^{1}}$ EEC = (ppm or ppb) in water

Risk Presumptions for Plants

Risk Presumption	RQ	LOC
Terrestr	ial and Semi-Aquatic Plants	
Acute High Risk	EEC¹/EC25	1
Acute Endangered Species	EEC/EC05 or NOAEC	1
	Aquatic Plants	
Acute High Risk	EEC ² /EC50	1
Acute Endangered Species	EEC/EC05 or NOAEC	1

¹ EEC = lbs ai/A

B. Aquatic Exposure and Risk Assessment

 $^{^2 \}frac{\text{mg/ft}^2}{\text{LD50 * wt. of bird}}$

³ mg of toxicant consumed/day LD50 * wt. of bird

² EEC = (ppm or ppb) in water

Approach Used for the Atrazine Ecological Risk Assessment

The atrazine aquatic risk assessment focuses mainly on aquatic plants and invertebrates and the potential for effects on sensitive plant species to result in community-level impacts which affect a range of aquatic organisms. The assessment is broken down by the type of water body (i.e., small static fresh water bodies such as ponds, flowing fresh water such as streams and rivers, larger bodies of fresh water such as lakes and reservoirs, and estuarine and marine habitats). Exposure for these three types of aquatic environments was estimated using PRZM-EXAMS modeling simulations (ponds) and monitoring data (streams, lakes and reservoirs, and estuarine/marine environments). Details on exposure are outlined for each type of aquatic environment.

EFED's initial assessment of aquatic risk, i.e., dividing modeled exposure concentrations by toxicity values from standard tests to generate risk quotients (RQs) which are then compared to levels of concern, will be confined to a standard pond scenario. The process used to assess risk for flowing fresh water, lakes and reservoirs, and estuarine and marine habitats will consider surface water monitoring data to estimate exposure and will use toxicity data taken principally from the open scientific literature.

1. Pond Assessment

Pond Exposures

No monitoring data were available for atrazine in ponds, therefore the assessment of risks to aquatic organisms in ponds is limited to the refined tier II approach with PRZM/EXAMS. The upper tenth percentile concentration values, expressed in Fg/L (ppb), are summarized below. The results of three uses, corn, sugarcane, and sorghum, were based on the standard scenarios provided by the Water Quality Tech Team (WQTT) to predict reasonable high exposure values, i.e., soils with high runoff potential and heavy rainfall amounts for maximum and typical use rates for aerial pre-plant, spray applications. The Annual Exceedence Probability graphs and data tables for maximum use rates can be found in Appendix V.

Information on maximum use rates are based on the Atrazine LUIS Report and labels. Data on acres treated, percent of crop treated and average application (typical) use rates are from BEAD's Quantitative Usage Analysis (dated May 10,1999). The maximum and typical use rates applied as an aerial spray applications of atrazine on Louisiana sugarcane are 4 and 2.6 lbs ai/A, respectively. Ohio corn are 2.0 and 1.1 lbs ai/A and Kansas sorghum are 2.0 and 1.2 lbs ai/A. The EECs used for the atrazine risk assessment for aquatic species in ponds are summarized in the following table.

Treated Crop	Maximum & Typical	Atrazine EEC Values ppb (Fg/L)				
	Use Rates (lb ai/A)	Peak Conc.	96-hour Average	21-day Average	60-day Average	90-day Average
Sugarcane	4.0	205	204	202	198	194
	2.6	133	133	131	129	126
Corn	2.0	38.2	38.0	37.2	35.5	34.2
	1.1	21.0	20.9	20.5	17.7	18.8
Sorghum	2.0	72.7	72.3	70.6	67.7	65.9
	1.2	43.6	43.4	42.4	40.6	39.5

The modeling results indicate that atrazine does have the potential to move into surface waters, especially for sugarcane use. Klassen and Kadoum (1979) found atrazine to be persistent in a farm pond ecosystem with estimated half-lives of six to eight months. These data are consistent with the persistence of atrazine seen in the gradual reductions in EEC levels produced by the PRZM-EXAMS model presented in the above table. With relatively stable atrazine concentrations in ponds, only small differences exist between simulated acute and chronic atrazine exposures for ponds, and the duration of the toxicity tests has little significance for assessing risks.

Monitoring data in the Upper Terrebonne watershed of Louisiana, an area with high sugarcane acreage, shows some atrazine levels in surface waters as high as $216 \, \text{Fg/L}$. This atrazine level supports and is consistent with the pond EECs ($205 \, \text{Fg/L}$) derived from the maximum use rate of $4.0 \, \text{lbs}$ ai/A on sugarcane.

The post-processor, LOAD.EXE, was used to estimate the chemical contributions of runoff, erosion and spray drift to the standard farm pond. The results expressed as percentages are tabulated below:

Percent of Pesticide Loadings from Different Sources to the Standard Pond

Use	Runoff	Erosion	Spray Drift
Corn	55.03%	3.47%	41.50%
Sugarcane	99.15%	0.85%	0.01%
Sorghum	71.80%	5.29%	22.91%

The erosion losses were the smallest among the three components, except for the sugarcane use scenario. Most of the atrazine losses to aquatic environments are from runoff, although spray drift also appears to have a large contribution in the corn scenario.

Pond Risk Quotients

The toxicity values used in the 1-hectare, 2-meter deep, pond risk assessments are limited to submitted studies using the standard toxicity endpoints. Normally, chronic risks are estimated using 96-hour and 21- to 90-day EECs, corresponding to the duration of the test, because it is uncertain when during the exposure the toxic effects are triggered. For atrazine, 21-day EECs were generally used for chronic exposures, because the difference in EEC values are so small. However, chronic risks to fish were estimated using 21-day and 90-day EECs, because the toxicity to fish in the full-life test increased at some later time compared to the results from the 28-day fish early-life stage test. The toxicity endpoints used in the pond risk assessment are included in Appendix XI: rainbow trout (*Onchorhynchus mykiss*) - acute, brook trout (*Salvelinus fontinalis*) - chronic, midge (*Chironomus tentans*) - acute, scud (*Gammarus fasciatus*) - chronic, duckweed (*Lemna gibba*) - 14 days (Hoberg 1993) and the algae (*Kirchneria subcapitata*) - acute (Hoberg 1993). Community-level atrazine effects on vascular plants, aquatic invertebrates populations and fish recruitment found in literature studies yield more sensitive endpoints and are discussed after the risk quotient assessment.

Risk Quotients for Sugarcane (Maximum Use Rate) (1 Pre-plant Aerial Application at 4.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	205 ppb	5,300 ppb	0.039				
Fish Reproduction NOAEC	194 - 202 ppb	65 ppb	2.9 - 3.1				
Aquatic Invertebrate Acute LC ₅₀	205 ppb	720 ppb	0.28				
Freshwater Invertebrate Reproduction NOAEC	202 ppb	60 ppb	3.4				
Freshwater Vascular Plant EC ₅₀	205 ppb	37 ppb	5.5				
Freshwater Algae EC ₅₀	205 ppb	49 ppb	4.2				

Risk Summary for a Maximum Pre-emergent Aerial Spray on Sugarcane: Atrazine aerially sprayed pre-emergence at 4.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity to aquatic plants (RQ = 1), restricted use for aquatic invertebrates (RQ = 0.1), and endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plants (RQ = 1.0 for the EC_{NOEC}).

The levels of concern for chronic effects ($\mathbf{RQ} = 1.0$) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from both the maximum use rate and the typical use rate for sugarcane and the NOAEC values for both fish and aquatic invertebrates. Chronic 21- to 90-day EECs ($\mathbf{194} - \mathbf{202} \, \mathbf{Fg/L}$) for the maximum use rates for sugarcane exceed the LOAECs for brook trout ($120 \, \mathbf{Fg/L}$ which reduced mean length by 7.2% and body weight by 16%), fathead minnow ($150 \, \mathbf{Fg/L}$ which reduced $\mathbf{F_1}$ length by 6.7% and body weight by 22%, *Gammarus fasciatus* ($140 \, \mathbf{Fg/L}$) which reduced the development of $\mathbf{F_1}$

to the seventh instar by 25%), and exceed the NOAEC values for *Chironomus tentans* (110 Fg/L) and *Daphnia magna* (140 Fg/L).

Risk Quotients for Sugarcane (Typical Use Rate) (1 Pre-plant Aerial Application at 2.6 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	133 ppb	5,300 ppb	0.025				
Fish Reproduction NOAEC 126 - 133 ppb 65 ppb 1.9 - 2.0							
Aquatic Invertebrate Acute LC ₅₀	133 ppb	720 ppb	0.18				
Freshwater Invertebrate Reproduction NOAEC 131 ppb 60 ppb 2.2							
Freshwater Vascular Plant EC ₅₀ 133 ppb 37 ppb 3.6							
Freshwater Algae FC	133 pph	49 ppb	2.7				

Risk Summary for a Typical Pre-emergent Aerial Spray on Sugarcane: Atrazine aerially sprayed pre-emergence at 2.6 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1), restricted use for aquatic invertebrates (RQ = 0.2), and endangered species for aquatic invertebrates (RQ = 0.05) and for aquatic vascular plants (RQ = 1.0 for the EC_{NOAEC}).

The levels of concern for chronic effects ($\mathbf{RQ} = 1.0$) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from both the maximum use rate and the typical use rate for sugarcane and the NOAEC values for both fish and aquatic invertebrates. Chronic 21- to 90-day EECs ($131 - 126 \, \mathrm{Fg/L}$) for the typical use rates for sugarcane exceed the LOAECs for brook trout ($120 \, \mathrm{Fg/L}$ which reduced mean length by 7.2% and body weight by 16%) and exceed the NOAEC values for bluegill sunfish ($95 \, \mathrm{Fg/L}$), Gammarus fasciatus ($60 \, \mathrm{Fg/L}$ and Chironomus tentans ($110 \, \mathrm{Fg/L}$).

Risk Quotients for Corn (Maximum Use Rate) (1 Pre-plant Aerial Application at 2.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	38.2 ppb	5,300 ppb	0.0072				
Fish Reproduction NOAEC 34.2 - 37.2 ppb 65 ppb 0.53 - 0.58							
Aquatic Invertebrate Acute LC ₅₀	38.2 ppb	720 ppb	0.053				
Freshwater Invertebrate Reproduction NOAEC	37.2 ppb	60 ppb	0.63				
Freshwater Vascular Plant EC ₅₀ 37.2 ppb 37 ppb 1.0							
Freshwater Vascular Plant EC _{NOEC}	37.2 ppb	< 3.4 ppb	> 11				

Freshwater Algae EC ₅₀	38.2 ppb	49 ppb	0.78

Risk Summary for a Maximum Pre-emergent Aerial Spray on Corn: Atrazine aerially sprayed pre-emergence at 2.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1.0) and for endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plants (RQ = 1.0 for the EC_{NOEC}). The risk quotients are freshwater fish acute (0.0072) and reproduction NOAEC (0.53-0.58), and aquatic invertebrate reproduction NOAEC (0.63) do not exceed levels of concern.

Risk Quotients for Corn (Typical Use Rate) (1 Pre-plant Aerial Application at 1.1 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	21.0 ppb	5,300 ppb	0.0040				
Fish Reproduction NOAEC	18.8 - 20.5 ppb	65 ppb	0.29 - 0.32				
Aquatic Invertebrate Acute LC ₅₀	21.0 ppb	720 ppb	0.029				
Freshwater Invertebrate Reproduction NOAEC	20.5 ppb	60 ppb	0.34				
Freshwater Vascular Plant EC ₅₀	20.5 ppb	37 ppb	0.56				
Freshwater Vascular Plant EC _{NOEC} 20.5 ppb < 3.4 ppb > 6.0							
Freshwater Algae EC ₅₀	21.0 ppb	49 ppb	0.43				

Risk Summary for a Typical Pre-emergent Aerial Spray on Corn: Atrazine aerially sprayed pre-emergence at 1.1 lbs ai/A yields a risk quotient that exceeds the level of concern for endangered species for aquatic vascular plants (RQ = 1 for the EC_{NOEC}). The risk quotients are freshwater fish acute (0.0040) and reproduction NOAEC (0.29-0.32), aquatic invertebrate acute (0.029) and reproduction NOAEC (0.34) do not exceed levels of concern.

Risk Quotients for Sorghum (Maximum Use Rate) (1 Pre-plant Aerial Application at 2.0 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	72.7 ppb	5,300 ppb	0.014				
Fish Reproduction NOAEC 65.9 - 70.6 ppb 65 ppb 1.0 - 1.1							
Aquatic Invertebrate Acute LC ₅₀	72.7 ppb	720 ppb	0.10				
Freshwater Invertebrate Reproduction NOAEC 70.6 ppb 60 ppb 1.2							
Freshwater Vascular Plant EC _{so}	72.7 ppb	37 ppb	2.0				

Freshwater Vascular Plant EC _{NOEC}	72.7 ppb	< 3.4 ppb	> 21
Freshwater Algae EC _{s0}	72.7 ppb	49 ppb	1.5

Risk Summary for a Maximum Pre-emergent Aerial Spray on Sorghum: Atrazine aerially sprayed pre-emergence at 2.0 lbs ai/A yields risk quotients which exceed the levels of concern for acute toxicity for aquatic plants (RQ = 1.0), restricted use for aquatic invertebrates (RQ = 0.1), and endangered species for aquatic invertebrates (RQ = 0.05) and aquatic vascular plant species (RQ = 1.0 for EC_{NOFC}).

The levels of concern for chronic effects ($\mathbf{RQ} = 1.0$) are exceeded by risk quotients for aquatic plants, fish and aquatic invertebrates based on the chronic EECs resulting from the maximum use rate for sorghum and the NOAEC values for both fish and aquatic invertebrates.

Risk Quotients for Sorghum (Typical Use Rate) (1 Pre-plant Aerial Application at 1.2 lbs ai/A) (Aquatic EEC's Based on PRZM-EXAMS Model)							
Species Exposure Toxicity Risk Quotient							
Freshwater Fish Acute LC ₅₀	43.6 ppb	5,300 ppb	0.0082				
Fish Reproduction NOAEC	39.5 - 42.4 ppb	65 ppb	0.61 - 0.65				
Aquatic Invertebrate Acute LC ₅₀	43.6 ppb	720 ppb	0.061				
Freshwater Invertebrate Reproduction NOAEC	42.4 ppb	60 ppb	0.71				
Freshwater Vascular Plant EC ₅₀	43.6 ppb	37 ppb	1.2				
Freshwater Vascular Plant EC _{NOEC} 43.6 ppb < 3.4 ppb > 13							
Freshwater Algae EC ₅₀	43.6 ppb	49 ppb	0.89				

Risk Summary for a Typical Pre-emergent Aerial Spray on Sorghum: Atrazine aerially sprayed pre-emergence at 1.2 lbs ai/A yields risk quotients that exceed the levels of concern for acute toxicity for vascular plants (RQ = 1) and endangered species for aquatic invertebrates (RQ = 0.05) and for aquatic vascular plants (RQ = 1 for EC_{NOEC}). The risk quotients for freshwater fish acute (0.0082) and reproduction NOAEC (0.61-0.65), aquatic invertebrate acute (0.061) and reproduction NOAEC (0.71) do not exceed levels of concern.

Evidence of Community-Level Pond Effects from Field Data

Results from artificial ponds in Kansas (Kettle *et al.*, 1987) treated with atrazine at 20 Fg/L provide evidence of significant community effects on aquatic organisms at concentrations substantially lower than the EECs for all of the above pond scenarios. The atrazine effects on the aquatic community included significant impacts on vascular plants (60 and 90% reductions in vegetation and the virtual loss of 3 plant species), aquatic invertebrates (reduced numbers and loss of some species as indicated by stomach contents), and fish (96% reduction in the number of

young bluegills).

Characterization of Atrazine Effects on Aquatic Plants

Many algal studies show 50% reductions in photosynthesis in 24 hours, 50% and higher reductions in chlorophyll production in one week, and 50% reductions in cell growth at water concentrations less than the peak EECs for **corn**, (maximum use rate and effects on a number of algal species below the typical, corn use, EECs (**20 Fg/L**) and all peak EECs for sorghum and sugarcane (Hoberg, 1991; Hughes, 1986; Parrish, 1978; Stratton and Corke, 1981; Torres and O'Flaherty, 1976). See Appendix XI for aquatic plant toxicity data.

Peak and chronic model-simulated EECs (**189 - 205** Fg/L) from atrazine use on **sugarcane** also exceed the EC₅₀ for growth on the vascular plants including duckweed (37, 43, 170, and 170 Fg/L), *Elodea canadensis* (80 Fg/L), Eurasian water-milfoil (91 Fg/L), and 50% reduction in oxygen production in *Potamogeton perfoliatus* at 30 Fg/L (Hoberg, 1993; Hoffman and Winkler, 1990; Kemp et al.,1985). Sugarcane EECs exceed acute effects on 14 algal species and chronic effects on an additional 2 algal species and 36 algal strains reported by Butler *et al.* (1975).

For **sorghum**, the peak and chronic model-generated EECs (**39.5 - 72.7 Fg/L**) exceed the EC₅₀ for growth on the vascular plants including duckweed (37 Fg/L; Hoberg, 1993) and non-growth effects on *Potamogeton perfoliatus* (30 Fg/L, 50% reduction in oxygen production; Kemp et al., 1985). Sorghum EECs exceed acute effects on 9 to 11 algal species, respectively and chronic effects on one additional algal species and 36 algal strains reported by Butler *et al.* (1975).

For the maximum use rate on **corn**, the peak and chronic modeled EECs (**34.2-38.2 Fg/L**) exceed the EC₅₀ for growth on the vascular duckweed (37 Fg/L), for non-growth effects on *Potamogeton perfoliatus* (30 Fg/L, 50% reduction in oxygen production), and exceed acute effects on 9 algal species and 2-week, chronic effects on 36 algal strains at 10 Fg/L reported by Butler *et al.* (1975). The typical use rate on corn yields peak and chronic EECs (**18.8 - 20 Fg/L**) exceed only the 2-week, chronic effects on 36 algal strains at 10 g/L reported by Butler *et al.* (1975).

Results from some freshwater microcosm studies at 5 Fg/L atrazine show slight, non-significant changes in the range or physical parameters such as reduced D.O. levels and pH levels and increased conductivity and alkalinity, but no significant effects on phytoplankton, zooplankton, or macro-invertebrates. Adverse effects on vascular plant primary productivity first appeared at about 10 Fg/L and at 15 Fg/L reductions occurred in copepod and rotifer densities after 7 days. Similar effects were reported for mesocosm studies: transient effects on water chemistry first appeared at < 0.1 to 10 Fg/L; at 1 Fg/L reductions in primary production and zooplankton numbers, and increases in bacterial numbers; at 10 to 68 Fg/L, reductions occurred in zooplankton populations, and 20 Fg/L, 60% reduction in macrophyte vegetation and elimination of 3 vascular species (Hoagland et al., 1993; Kettle et al., 1987)

Conclusion: Based on standard acute and chronic toxicity and the standard 2-meter deep pond

adjacent to treated-sorghum and sugarcane fields, atrazine EECs exceed levels of concern for direct effects on fish and aquatic invertebrate reproduction and freshwater vascular plants and algae. Atrazine EECs from applications to corn do not exceed levels of concern for fish or aquatic invertebrates, but corn EECs do exceed levels of concern for some algal species.

Atrazine use on the above crops is estimated to yield surface water concentrations which exceed a number of non-standard, sublethal toxicity levels reported in the literature for a number of fish species and exceed concentrations which have indirect community effects on aquatic species. Indirect effects on fish and aquatic invertebrates are severe due to the loss of 60 to 95 percent of the vegetative cover, which provides habitat to conceal young fish and aquatic invertebrates from predators.

Direct effects of atrazine to nontarget aquatic plants indicate high risk. Numerous reports attest to atrazine's ability to inhibit photosynthesis, change community structure, and cause the mortality of aquatic flora at concentrations between 20 and 500 Fg/L (deNoyelles and Kettle 1980; deNoyelles *et al.* 1982; Dewey 1986; Kettle *et al.* 1987).

2. Lake and Reservoir Risk Assessment

Endpoints Used to Assess Aquatic Risk

A general discussion of atrazine's acute and chronic toxicity to aquatic organisms can be found in Section III (Integrated Risk Characterization). The table below summarizes the key endpoints used to assess aquatic risk based on atrazine monitoring data:

Table ____. Key Endpoints for the Lentic Freshwater Environment (e.g., reservoirs, lakes). The Endpoints Chosen to Drive the Risk Assessment are Highlighted.

Key Group of Non- target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
Fish	Lab	Acute Fish (96- hours) LC50 = 53,000 Fg/L	Rainbow trout / Mortality	00024716 Beliles & Scott 1965	Fish Mortality Estimated to Occur at 53,000 F g/L
	Lab	Chronic Fish (44- weeks) NOAEC = 65 F g/L	Brook trout / [7.2 % red. mean length, 16 % red. mean body weight]	00024377 Macek et al. 1976	Reduction in Fish Growth Estimated to Occur at 65 F g/L
	Field (mesocosms)	96% Reduction in # of Young Fish Occurred at 20 Fg/L (Caused by Loss of Food and Habitat)	Bluegill sunfish	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Fish Population Reduction Likely to Occur at 20 Fg/L due to Loss of Food and Habitat
Invertebrates	Lab	Acute Invertebrate (48-hour) LC ₅₀ = 720 F g/L	Midge / Mortality	00024377 Macek <i>et</i> <i>al</i> . 1976	Invertebrate Mortality Estimated to Occur at 720 Fg/L

Key Group of Non- target Organisms	Type of Study	Measurement Endpoint	Test Organisms / Effect	Citation [MRID# Author & Date]	Assessment Endpoint
	Lab	Chronic Invertebrate (48-hour) NOAEC = 60 F g/L	Scud / [25 % red. in development of F ₁ to seventh instar]	00024377 Macek et al. 1976	Reduction in Invertebrate Populations Estimated to Occur at 60 F g/L
Invertebrates	Field	59-65% Reduction in Daphnid population growth occurred at 10 Fg/L over 18- days	Daphnids	45087414 Lampert <i>et</i> <i>al.</i> 1989	Invertebrate Populations Likely to be Reduced at 10 Fg/L
Non-Vascular Plants	Lab	Acute Algae (1-week) $EC_{50} = 1 Fg/L$	Four species [41-93% reduction in chlorophyll production]	00023544 Torres & O'Flaherty 1976	Reduction in Primary Production Estimated to Occur at 1 Fg/L
	Microcosm	23% Reduction in gross primary production 10 Fg/L (at day 2); recovery by day 7	phytoplankton	45087413 Johnson 1996	Reduction in Primary Production Estimated to Occur at 10 Fg/L
	Field	42% Reduction in phytoplankton biomass (at days 2-7) occurred at 20 Fg/L	phytoplankton	45020011 DeNoylles et al. 1982	Reduction in Primary Production Likely to Occur at 20 Fg/L
Vascular Plants	Lab	Acute (14-days) EC _{s0} = 37 Fg/L	Duckweed [50% reduction in growth]	43074804 Holberg 1993	Reduction in Macrophytes Estimated to Occur at 37 Fg/L
Vascular Plants	Mesocosm	60% Reduction of macrophyte vegetation occurred at 20 F g/L (at summers end; also, loss of three species); by May of following year, 95% Reduction of of macrophyte vegetation	Macrophytes	45202912 Kettle, de Noyelles, Jr., Heacock and Kadoum 1987	Reduction in Macrophytes (number & diversity) Likely to Occur at 20 Fg/L

For a refined discussion of risk to lakes and reservoirs, see Section III above.

3. Stream Risk Assessment

See Section III above.

4. Estuarine Risks

See Section III.

c. Terrestrial Risk Assessment

1. Animal Risk Assessment

Acutely, atrazine is practically non-toxic to birds and mammals. Risks from atrazine uses on sugarcane, corn and sorghum are assessed for maximum and typical use rates using the typical risk assessment methodology. Given the maximum use rate of 4 lbs ai per acre on sugarcane, the upper limit atrazine exposure levels would be about **960 ppm** on short grass and **540 ppm** on foliage in the treated field and along the field edges. The residue levels on insects are assumed to be **15 and 135 ppm per lb ai/acre** for large and small insects, respectively. The mammalian acute toxicity value used in the assessment is based on the rat LD₅₀ (**1,869 mg/kg**). The mammalian LOAEL (500 ppm) significantly reduced adult rat body weight and adult food consumption (**NOAEL 50 ppm**). At 50 ppm, second generation rat pups had significantly reduced body weight (**NOAEL, 10 ppm**). The LOAELs for bobwhite and mallard ducks were 225 ppm, based on 29 and 49% reductions in egg production, respectively (**NOAEL, 225 ppm**). Risk quotients are provided for a range of appropriate food items for each animal group in the following tables for atrazine applications on sugarcane, corn and sorghum.

In order to determine the length of time that levels of concern would be exceeded following applications, a conservative foliar half-life was estimated from the following atrazine residue data. Based on transferable residue data from atrazine-treated turf, the atrazine half-lives for sprays are 5.2 ± 0.22 , 15.6 ± 0.86 and 17 ± 0.18 days in Georgia, 3.2 ± 0.81 , 3.3 ± 0.80 and 3.8 ± 0.87 days in North Carolina. For granular applications, the atrazine half-lives are 4.9 ± 0.91 days (no irrigation) and 6.0 ± 0.69 days (after irrigation) in Florida and 6.8 ± 0.91 days (no irrigation) and 10.5 ± 0.41 days (after irrigation) in Georgia. These data indicate fairly high variation in atrazine half-lives (i.e., from 3.2 ± 0.17 days). An atrazine, foliar half-life of 17 days will be used as a conservative estimate for dietary assessment of risks for avian and small mammals. The Terrestrial Fate Residue model was used to estimate the daily residue levels. Appendix IX contains the documentation of the method, the equation and examples for atrazine.

(Pre-plant, Ac	Risk Quotients for Maximum Use Rate on Sugarcane (Pre-plant, Aerial Spray; 1 Application at 4.0 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)					
Surrogate Species Exposure Toxicity Risk Quotient						

Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 - 960 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.031 - 0.49 0.021 - 0.34 0.0048 - 0.077
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 - 540 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.031 - 0.27 0.021 - 0.19 0.0048 - 0.043
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	60 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0067 0.0048 0.00096
Mammalian Reproduction NOAEL	60 - 960 ppm	10 ppm	6.0 - 96
Avian Subacute Dietary LC ₅₀	60 - 960 ppm	> 5,000 ppm	< 0.012 < 0.19
Avian Reproduction NOAEL	60 - 960 ppm	225 ppm	0.27 - 4.3

Risk Summary for the Maximum Sugarcane Spray Use: Risk quotients derived for a single application at the typical use rate of 4.0 lbs ai/A on sugarcane exceed the levels of concern for restricted use ($\mathbf{RQ} = \mathbf{0.2}$) for small and medium-sized herbivores and small insectivores, and endangered species ($\mathbf{RQ} = \mathbf{0.1}$) for small and medium-sized herbivores and insectivores.

Chronic level of concern (**RQ** = **1.0**) is exceeded for mammalian and avian reproduction. The maximum atrazine level on short grass (**960 ppm**) exceeds the chronic LOAEL values for both bobwhite and mallards and the mammalian LOAEL for rats. At 675 ppm, adverse effects on bobwhite included: 29% reduction in egg production, a 67% increase in defective eggs, a 27% reduction in embryo viability, a 6 to 13% reduction in hatchling body weight, and a 10 to 16% reduction in 14-day old bobwhite body weight (Pedersen and DuCharme, 1992). At 675 ppm, adverse effects on mallards included reductions of 49% in egg production, 61% in egg hatchability and 12 to 17% in adult food consumption (Pedersen and DuCharme, 1992). The mammalian reproductive **NOAELs** (**50 ppm**, for reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded.

Based on a conservative, foliar half-life of 17 days and maximum atrazine levels on short grass and broadleaf foliage, atrazine residues would exceed the avian reproductive **NOAELs** (225 **ppm**) for 35 and 21 days, respectively. The mammalian reproductive **NOAELs** (50 **ppm**), reduction in adult body weight and food consumption) and (10 **ppm**), reduction in second generation pup body weights) are exceeded on grass for 72 and 111 days, respectively and on broadleaf foliage for 58 and 97 days, respectively.

Spray drift onto vegetation in areas surrounding a treated field (i.e., field borders and riparian areas next to streams) using the standard, 5 percent spray drift value for aerial applications would appear to yield atrazine levels which do not pose a reproductive risk to birds and pose low chronic risks to small mammals. At 4 lbs ai/A, maximum atrazine levels on grass are 48 ppm and 27 ppm on broadleaf foliage; at 2 lbs ai/A, atrazine levels are 24 ppm on grass and 13.5 ppm on broadleaf foliage. Based on these spray drift exposures, atrazine would exceed only the NOAEC of 10 ppm for rat pup body weight reductions for 21 days. These risks to wildlife will

be reassessed when peer review of the Ag Drift Model is completed and approved.

Risk Quotients for Typical Use Rate on Sugarcane (Pre-plant, Aerial Spray; 1 Application at 2.6 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)							
Surrogate Species Exposure Toxicity Risk Quotient							
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 - 624 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.020 - 0.32 0.014 - 0.22 0.0031 - 0.050				
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 - 151 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.020 - 0.08 0.014 - 0.053 0.0031 - 0.012				
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	39 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0044 0.0031 0.00063				
Mammalian Reproduction NOAEL	39 - 624 ppm	10 ppm	3.9 - 62				
Avian Subacute Dietary LC ₅₀	39 - 624 ppm	> 5,000 ppm	< 0.0078 < 0.12				
Avian Reproduction NOAEL	39 - 624 ppm	225 ppm	0.17 - 2.8				

Risk Summary for Typical Sugarcane Spray Use: Risk quotients derived for a single application at the typical use rate of 2.6 lbs ai/A on sugarcane exceed the levels of concern for restricted use ($\mathbf{RQ} = \mathbf{0.2}$) for small and medium-sized herbivores and for endangered species ($\mathbf{RQ} = \mathbf{0.1}$) for small and medium-sized herbivores.

Chronic level of concern ($\mathbf{RQ} = 1.0$) is exceeded for mammalian and avian reproduction NOAECs. Typical atrazine levels on short grass (624) exceeds the chronic NOAEL values for both bobwhite and mallards and the mammalian NOAEL for rats.

Risk Quotients for Maximum Use Rate on Corn and/or Sorghum (Pre-plant, Aerial Spray; 1 Application at 2.0 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)							
Surrogate Species Exposure Toxicity Risk Quotient							
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 - 480 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.015 - 0.24 0.010 - 0.17 0.0024 - 0.039				
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 - 270 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.015 - 0.14 0.010 - 0.095 0.024 - 0.022				
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	30 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.034 0.0024 0.00048				
Mammalian Reproduction NOAEL	30 - 480 ppm	10 ppm	3.0 - 48				

Avian Subacute Dietary LC ₅₀	30 - 480 ppm	> 5,000 ppm	< 0.0060 < 0.096
Avian Reproduction NOAEL	30 - 480 ppm	225 ppm	0.13 - 2.1

Risk Summary for Maximum Corn and Sorghum Spray Use: Risk quotients derived for a single application at the maximum use rate of 2.0 lbs ai/A on corn or sorghum exceed the levels of concern for restricted use ($\mathbf{RQ} = \mathbf{0.2}$) for small mammalian herbivores and for endangered species ($\mathbf{RQ} = \mathbf{0.1}$) for small mammalian herbivores and insectivores.

Chronic level of concern (**RQ** = **1.0**) is exceeded for mammalian and avian reproduction. Maximum atrazine levels on short grass (**480 ppm**) exceed the chronic LOAEL value for bobwhite chicks and the NOAECs (225 ppm) for bobwhite and mallard ducks for 35 days. The mammalian reproductive **NOAELs** (**50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for 54 and 94 days, respectively for maximum residue levels on short grass.

Based on these spray drift exposures, atrazine would exceed only the NOAEC of 10 ppm for rat pup body weight reductions for 7 days. These risks to wildlife will be reassessed when peer review of the Ag Drift Model is completed and approved.

Risk Quotients for the Typical Use Rate on Corn (Pre-plant, Aerial Spray; 1 Application at 1.1 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)						
Surrogate Species	Exposure	Toxicity	Risk Quotient			
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 - 264 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0084 - 0.13 0.0058 - 0.093 0.0013 - 0.021			
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 - 148.5 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0084 - 0.075 0.0058 - 0.052 0.0013 - 0.012			
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	16.5 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0019 0.0013 0.00026			
Mammalian Reproduction NOAEL	16.5 - 264 ppm	10 ppm	1.6 - 26			
Avian Subacute Dietary LC ₅₀	16.5 - 264 ppm	> 5,000 ppm	< 0.0033 < 0.053			
Avian Reproduction NOAEL	16.5 - 264 ppm	225 ppm	0.73 - 1.2			

Risk Summary for Typical Corn Spray Use: Risk quotients derived for a single application at the typical use rate of 1.1 lbs ai/A on corn exceed the levels of concern for restricted use ($\mathbf{RQ} = \mathbf{0.2}$) and for endangered species ($\mathbf{RQ} = \mathbf{0.1}$) for small mammalian herbivores.

Chronic level of concern ($\mathbf{RQ} = 1.0$) is exceeded for mammalian and avian reproduction.

Maximum atrazine levels on short grass (**264 ppm**) exceed the chronic LOAEL value for bobwhite and the NOAECs (225 ppm) for bobwhite and mallard ducks for about 4 days. The mammalian reproductive **NOAELs** (**50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for about 40 and 80 days, respectively, based on maximum residue levels on short grass.

Risk Quotients for the Typical Use Rate on Sorghum (Pre-plant, Aerial Spray; 1 Application at 1.2 lbs ai/A) (Terrestrial EEC's Based on Fletcher <i>et al.</i> , 1994)						
Surrogate Species	Exposure	Toxicity	Risk Quotient			
Mammalian Herbivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 - 288 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0092 - 0.15 0.0064 - 0.10 0.0014 - 0.023			
Mammalian Insectivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 - 162 ppm	1,967 ppm 2,832 ppm 12,460 ppm	0.0092 - 0.082 0.0064 - 0.057 0.0014 - 0.013			
Mammalian Granivores LD ₅₀ (15 grams body wt.) (35 grams body wt.) (1000 grams body wt.)	18 ppm	8,900 ppm 12,460 ppm 62,300 ppm	0.0020 0.0014 0.00029			
Mammalian Reproduction NOAEL	18 - 288 ppm	10 ppm	1.8 - 29			
Avian Subacute Dietary LC ₅₀	18 - 288 ppm	> 5,000 ppm	< 0.0036 < 0.058			
Avian Reproduction NOAEL	18 - 288 ppm	225 ppm	0.08 - 1.1			

Risk Summary for Typical Sorghum Spray Use: Risk quotients derived for a single application at the typical use rate of 1.2 lbs ai/A on sorghum exceed the levels of concern for endangered species ($\mathbf{RQ} = \mathbf{0.1}$) for small and medium-sized mammalian herbivores.

Chronic level of concern (**RQ** = **1.0**) is exceeded for mammalian and avian reproduction. Atrazine residue levels on short grass (**288 ppm**) exceed the chronic NOAECs for bobwhite and mallard ducks for about 5 days. The mammalian reproductive **NOAELs** (**50 ppm**, reduction in adult body weight and food consumption) and (**10 ppm**, reduction in second generation pup body weights) are exceeded for 42 and 90 days, respectively for maximum residue levels on short grass.

Historically, herbicides have had a much different effect on animal populations than insecticides. Insecticides generally affect animal populations via direct lethality (e.g., carbofuran, chlorpyrifos, guthion, etc.) and/or severe reproductive impairment (e.g., DDT/DDE). If the insecticide-treated area is favorable habitat for one or more species, following the death of the resident species, other animals may quickly reoccupy the treated site and may or may not also succumb to poisoning from the pesticide. Herbicide effects on wildlife are not normally mortality. Rather the herbicide alters the habitat and makes it no longer suitable for a species. The herbicide can alter the types of vegetation or reduce food sources in the habitat such that the

animal must move elsewhere and possibly to a less suitable area. Thus, herbicides affect animal populations by reducing favorable habitat and increasing competition among species for nesting and food resources. In as much as essential vegetation in treated areas, such as right-of-ways, field margins and riparian areas are affected by spray drift and/or runoff, some bird and/or small mammal species may be forced to seek new areas for feeding, nesting and survival.

2. Plant Risk Assessment

a. Spray Drift and Runoff Assessments

Atrazine applications to crop and non-crop areas pose an exposure to non-target plants in areas adjacent to treated fields via spray drift and runoff. Standard EFED values were used for spray drift and runoff levels. Spray drift levels for ground and aerial applications are 1 and 5 percent, respectively. Atrazine is highly mobile in soils and has a low soil-water partitioning coefficient and a water solubility value of about 33 ppm. Its runoff is estimated at 2 percent. The scenario for plants growing in dry areas receive runoff from 1 hectare to 1 hectare, while a 1-hectare wet area receives runoff from 10 hectares. All plant toxicity values are present as pounds active ingredient per acre (lbs ai/A). The EC₂₅ values are used to calculate risk quotients for the typical non-target plants and the NOAEC values are used for endangered and threatened plant species. The formulae for deriving EECs for plants are given in Appendix X. The following tables present risk quotients for non-target terrestrial plants following at-plant, aerial and ground applications of 4 lbs ai/A, which is the maximum application rate for atrazine (i.e., sugarcane). Assuming a 60 percent aerial spray efficiency, the exposure values used to assess risks for 4 lbs ai/A are 0.2 lbs ai/A for aerial spray drift, 0.248 lbs ai/A for both spray drift and runoff to dry areas, and 0.68 lbs ai/A for spray drift and runoff to wet areas. All risk quotients are rounded off to two significant digits.

	Atrazine Risk	Quotients for Terres	strial Plants (4 lbs ai.	/A; Aerial Applicatio	n)
Crop	Spray Drift (5%)		Spray Drift + Runoff to Dry and Wet Areas		
	Vegetative Vigor EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species	Seedling Emergence EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species in Dry Areas	Risk Quotients Typical/Endangered Species in Wet Areas
Carrot	1.7 / 2.0	0.12 / 0.10	0.003 / 0.0025	83 / 99	230 / 270
Oats	2.4 / 2.0	0.083/ 0.10	0.004 / 0.0025	62 / 99	170 / 270
Ryegrass	>4.0 />4.0	<0.05 /<0.05	0.004 / 0.005	62 / 50	170 / 140
Lettuce	0.33 / 0.25	0.61 / 0.80	0.005 / 0.005	50 / 50	140 / 140
Onion	0.61 / 0.5	0.33 / 0.40	0.009 / 0.005	28 / 50	76 / 140
Cucumber	0.008/ 0.005	25 / 40	0.013 / 0.005	19 / 50	52 / 140
Soybean	0.026/ 0.02	7.7 / 10	0.19 / 0.025	1.3 / 9.9	3.5 / 27
Cabbage	0.014/ 0.005	14 / 40	0.014 / 0.01	18 / 25	49 / 68

Tomato	0.72 / 0.5	0.28 / 0.40	0.034 / 0.01	7.3 / 25	20 / 68
Corn	>4.0 / >4.0	< 0.05/<0.05	> 4.0 / > 4.0	<0.062/<0.062	<0.17 /<0.17

The levels of concern for terrestrial plants are exceeded for acute risk (RQ = 1.0) and endangered plant species (RQ = 1.0). Three out of the ten crops (i.e., cucumber, soybeans, and cabbage) are at risk from spray drift, if planted adjacent to atrazine-treated sugarcane. Of the ten crops, only corn is not at risk from combined spray drift and runoff exposures.

Assuming 100 percent ground spray, application efficiency, the exposure values used to assess risks for 4 lbs ai/A are 0.04 lbs ai/A for aerial spray drift, 0.12 lbs ai/A for both spray drift and runoff to dry areas, and 0.84 lbs ai/A for spray drift and runoff to wet areas. All risk quotients are rounded off to two significant digits.

Atrazine Risk Quotients for Terrestrial Plants (4 lbs ai./A; Ground Application)						
Crop	Spray I	Drift (1%)	Spray Drift + Runoff to Dry and Wet Areas			
	Vegetative Vigor EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species	Seedling Emergence EC ₂₅ /NOAEC (lbs ai/A)	Risk Quotients Typical/Endangered Species in Dry Areas	Risk Quotients Typical/Endangered Species in Wet Areas	
Carrot	1.7 / 2.0	0.024/ 0.02	0.003 / 0.0025	40 / 48	280 / 340	
Oats	2.4 / 2.0	0.017/ 0.02	0.004 / 0.0025	30 / 48	210 / 340	
Ryegrass	>4.0 />4.0	<0.01 /<0.01	0.004 / 0.005	30 / 24	210 / 170	
Lettuce	0.33 / 0.25	0.12 / 0.16	0.005 / 0.005	24 / 24	170 / 170	
Onion	0.61 / 0.5	0.066/ 0.08	0.009 / 0.005	13 / 24	93 / 170	
Cucumber	0.008/ 0.005	5.0 / 8.0	0.013 / 0.005	9.2 / 24	65 / 170	
Soybean	0.026/ 0.02	1.5 / 2.0	0.19 / 0.025	0.63 / 4.8	4.4 / 34	
Cabbage	0.014/ 0.005	2.9 / 8.0	0.014 / 0.01	8.6 / 12	60 / 84	
Tomato	0.72 / 0.5	0.056/ 0.08	0.034 / 0.01	3.5 / 12	25 / 84	
Corn	>4.0 / >4.0	< 0.01/<0.01	> 4.0 / > 4.0	<0.03 /<0.03	<0.21 /<0.21	

Three out of the ten non-target crop species (i.e., cucumbers, soybeans and cabbage, which are all dicots) are at risk from spray drift alone, if grown adjacent to atrazine-treated sugarcane ground sprayed with 4 lbs ai/A, the maximum registered use rate.. The combination of spray drift and runoff poses risks to eight out of the ten crops if grown in dry habitats and to nine out of ten crops if grown in low-lying, semi-aquatic habitats.

A ground application of 2 lbs ai/A to corn and/or sorghum poses a diminished risk to adjacent crops compared to 4-lb ai/A applications to sugarcane, but only one of these species (i.e., soybeans from spray drift) would no longer exceed the acute level of concern. At the typical corn use rate of 1.1 lbs ai/A, the non-target crops at risk are cucumbers from spray drift (RQ =

1.4), 7 out of 9 non-target species growing in dry habitats, and all 9 non-target species, if grown in semi-aquatic habitats. Risk quotients for endangered plant species indicate concern for endangered species growing in areas adjacent to atrazine-treated fields from combined spray drift and runoff.

Non-target terrestrial plants in adjacent fields or habitats are potentially at risk from spray drift and from runoff for all registered uses. The level of concern for endangered terrestrial plant species is exceeded for both monocots and dicots and the concerns need to be addressed by the registrant.

b. Atmospheric Deposition Assessment

Volatility as a route of field dissipation raises concerns about the atmospheric fate of atrazine, its aerial transport and whether aerial deposition poses the potential for risks to non-target terrestrial plants. The Lake Michigan Mass Balance study monitors all sources of inputs into Lake Michigan, including atmospheric inputs. In the 1970's and 1980's, atmospheric inputs were reported to be 24 percent of the total atrazine input into Lake Michigan and in the 1990's the atmospheric contribution was 29 percent (Russell Kreis, US EPA, Great Lakes National Program Office, Region 5; personal communication, dated 11/07/2000). The potential for adverse effects on sensitive, non-target crops and plants from atmospheric deposition is uncertain. It is reasonable to assume that rainfall represents a similar route(s) of exposure to terrestrial plants as spray drift and the spray applications used in the vegetative vigor tests. Levels of concern for terrestrial plants were calculated, using the lowest vegetative vigor EC₂₅ and NOAEC values. The lowest vegetative vigor values are an EC₂₅ of 0.008 lbs ai/A for cucumber and the NOAEC for endangered species is 0.005 lbs ai/A for cucumbers and cabbage. Assuming rainfall events of 0.25 and 0.5 inches, atrazine concentrations of concern in rainfall were calculated to be 140 and 88 Fg/L and 70 and 44 Fg/L, respectively. The following formula was used to calculate the levels of concern for atrazine levels in 0.25 and 0.5 inches of rain.

Fg/L pesticide =
$$\frac{\text{EC or NOAEC (lb/ac)} \times 453.59 \text{ (g/lb)} \times 1000 \text{ (cm}^3/\text{L)}}{\text{x (ac/0.4069 ha)} \times (\text{ha/10e8 cm}^2) \times 10e6 \text{ (ug/g)}}$$
depth of rainfall (in) x 2.54 (cm/in)

Atrazine concentrations in rainfall have been measured up to 3.5 Fg/L in Germany (Braun *et al.*, 1987). In 1990-1991, the 95th and 99th percentile atrazine levels in rainfall in the mid-west were reported to be 0.42 and 1.0 Fg/L, respectively (USGS Fact Sheet FS-181-97). Capel *et al.* (1994) reported the frequency of detections and pesticide levels in rainfall from 1991 to 1993 in Minnesota; in 1991, atrazine was detected in 2 % of the samples with a maximum concentration of 0.82 Fg/L, in 1992 it was 18 percent and 2.2 Fg/L, and in 1993 it was 71 % and 2.9 Fg/L. Subsequent 1994 monitoring data from 6 Minnesota sites around the state found detections in 93% of the samples (range: 86 - 100%) and a maximum level of 2.8 Fg/L (range of maximum levels: 0.74 - 2.8 Fg/L). Atrazine concentrations in rainfall monitored in the Lake Michigan study ranged from ND to about 400 ng/L. At one Lake site, much higher atrazine levels were believed to be an outlier (Russell Kreis, e-mail on 11/07/2000). Logic would suggest that

atrazine concentrations in rainfall near Lake Michigan would be higher than the rainfall levels in Minnesota. Higher atrazine levels in rainfall would be consistent with the lake's proximity to and the prevailing winds from the corn belt just to the west and south, where USGS (Fact Sheet FS-181-97) has indicated the highest US poundage use of atrazine per square kilometer in the northern parts of Illinois and Indiana.

Russell Kreis (e-mail on 11/09/2000) wrote "The high concentration [the outlier] I spoke of was at Indiana Dunes (- 2800 ng/L) and is proximal to one of the high usage areas you spoke of. This concentration was not reproduced in 1995 and the volume collected at that time was noted to be 3 times lower than other samples. Thus the suspicion that it was an outlier." Kreis's conclusion would appear to be inconsistent with my understanding that the first rain drops wash most of the "chemicals" and particulates out of the atmosphere. Subsequent rain during the same rainfall event would add some additional "material," but any additional rain would dilute the higher concentrations present in the initial raindrops. It would appear that the "outlier" sample which is one-third the volume of other samples, represents the first rain drops with the maximum atrazine concentrations. In addition, the 1994 Indiana Dunes rainfall sample (2,800 ng/L or 2.8 Fg/L) is consistent with the Minnesota data for maximum atrazine concentrations in rainfall reported in 1993 (2.9 Fg/L) and 1994 (2.8 Fg/L) and would not appear to be an outlier.

The Minnesota data for atrazine between 1991 and 1994 indicate a gradual increase in both the frequency of detection and the maximum concentration. Lake Michigan rainfall data also indicate increasing atrazine levels in rainfall from the 1970's through the 1980's and 1990's. Latest available data on atrazine concentrations in rainfall is from Lake Michigan in 1996.

Seedling emergence toxicity data could be also be used to assess toxic effects of atrazine on terrestrial plants based on total mass of atrazine added to the soil from rainfall. For this calculation, rainfall data would require knowing the total mass of atrazine in the rainfall (e.g., the mean concentration (Fg/L) and amount of rainfall (cm)). Levels of concern for terrestrial plants and endangered plant species were calculated, using the lowest seedling emergence EC₂₅ and NOAEC values from soil watering treatments. The lowest vegetative vigor values are an EC₂₅ of 0.003 lbs ai/A for carrot and 0.004 lbs ai/A for oats and ryegrass and the NOAECs for endangered species are 0.0025 lbs ai/A for carrots and oats, and 0.005 lbs ai/A for onion, ryegrass, lettuce and cucumbers. Atrazine levels of concern in rainfall were calculated to be 0.034 and 0.045 Fg/cm² and 0.028 and 0.056 Fg/cm², respectively. The following formula was used to calculate total mass of atrazine of concern in rainfall.

Mass in rainfall (F g/cm²) = EC_{25} (or NOAEC) lbs ai/acre x 11.21 F g/cm² / lb ai/acre

If the rainfall contains 50 Fg/L, the depth of rainfall needed to exceed levels of concern for the carrot EC_{25} (0.003 lbs ai/A = 0.034 Fg/cm²) and NOAEC (0.0025 lbs ai/A = 0.028 Fg/cm²) are 0.68 cm (i.e., 1.7 inches) for sensitive terrestrial plants and 0.56 cm (i.e., 1.4 inches) for endangered plant species. Since pesticide concentrations in rain are not likely to be a linear function of the amount of rainfall, it is unclear whether rainfall equal to or greater than 1.4 inches would have a mean atrazine concentration of 50 Fg/L or whether atrazine levels in

rainfall occur higher than 50 Fg/L.

Based on toxicity data, aerial deposition of atrazine at concentrations up to 50 would not appear to be a risk to birds, mammals, fish, aquatic invertebrates and aquatic vascular plants. Risks to non-target terrestrial plants from rainfall based on the most sensitive vegetative vigor and seedling emergence test data are uncertain. If the mean atrazine concentration in rainfall does not exceed 50 Fg/L and the amount of rainfall does not reach 1.4 inches, there would appear to be no risks to non-target terrestrial plants, based on seedling germination toxicity data. Based on the NOAEC values for risks to endangered species, a rainfall event with an atrazine concentration of 50 Fg/L would exceed the level of concern of 44 Fg/L using the most sensitive vegetative vigor, NOAEL value (i.e., 0.005 lbs ai/A) for cucumbers and cabbage.

d. Incident Reports

A number of incidents have been reported in which atrazine has been associated with some type of environmental effect with variable levels of certainty ranging from unlikely to highly probable. As of October 26, 2000, 109 incidents were listed in the Ecological Incident Information System (EIIS) files under atrazine: 4 cases are listed as highly probable, 40 as probable, 50 as possible, 13 as unlikely, and 2 as unrelated. Atrazine alone is not very toxic to the birds, mammals, and aquatic animals cited in most of these incidents. In none of these cases has evidence been provided that firmly demonstrate that atrazine has produced the reported effects. In only one incident (# I004021-004) was analytic analyses of the fish made for atrazine; many chemicals were identified and high profenofos levels were found in the fish and the organophosphate was determined to be responsible for the large fish kill. In many cases, the inference of these reported incidents to atrazine effects is likely do to the wide spread use of atrazine and the proximity of the atrazine application and timing to the occurrence to the incident. Having said this, synergism and indirect effects could explain how atrazine could have caused some of these incidents.

The majority of the incidents (about 40 percent of the "probable" cases) are listed as effects on corn mostly from corn applications. A number of the crop losses are large (50, 55, 56, 75 percent and a few "All" cases); other incidents cited acres lost: (3, 8, 12, 15, 17, 18, 18, 20, 50, 50, 50, 55, 60, 65, 65, 71, 80, 80, 82, 90, 100, 155, 240, 596, and 631 acres).

Forty incidents are considered "Probable," and four incidents are listed as "Highly Probable." The 4 incidents listed as "Highly Probable" include 3 home/lawn use incidents and 1 corn use incident. The corn use incident reported affecting 100 bass and 100 bream (# B000163-001) resulting from registered use. The three home/lawn incidents were lawn applications which affected grass; two were concluded to be misuse/accidental (# I005579-001, I005132-001). The third home incident (# I001910) was a registered EC use which affected grass and non-target plants.

The forty "Probable" incidents include: 16 (40 %) cases affecting corn; 11 (27.5 %) affecting grass; 11 (27.5 %) fish kills; 1 bird kill case; and affects on ornamentals (2 cases), fruit trees (2

cases), berries (1), garden (1), oats (1), runoff killed vegetation around an atrazine/cyanazine-treated field and pond irrigation water killed greenhouse plants. Four "probable" incidents are classified as misuse (accidents): two cases from corn use (I005879-003, pears, raspberry and oats and I007371-013, grass and ornamentals); and two lawn misuse cases: I009445-031, grass; and I009445-029, bluegrass.

Analysis of 14 corn incidents occurring in 1999 which were submitted by Novartis indicates that in all cases, formulations of Bicep II (a mixture of atrazine and metolachlor) were used. The reported applications rates ranged from 1.4 quarts of atrazine /1.4 quarts of metolachlor to 2.6/2.6 quarts/A. Effects included distorted and cupping leaves, failure to unfurl, uneven height, chlorotic yellowing and necrotic leaves, and killed. Corn acreage affected ranged from 55 to 55 percent of 600 acres. There were 11 grass incidents resulting from home/lawn uses; three of these cases are considered to misuse (accidental).

Many fish species have been killed in these atrazine incident reports, including: bluegills, largemouth bass, catfish, quillback carpsucker, carp, redhorse, shad, bream, garfish, perch, minnows and crappie. In some incidents very large numbers of fish have been killed. Among the fish kill incidents classified as possible to highly probable, the following large fish kills and the state have been reported: a thousand bluegill and a thousand largemouth bass (DE: # I000116-002), 300 largemouth bass and 300 bluegill (DE: # B0000-300-28), 600 catfish (IL: # I001081-001), a thousand quillback carpsucker, a thousand carp and a thousand redhorse suckers (IL: # I005002-006), 100 bass and 100 bream (SC: # B000163-001), 2,000 perch (WA: #I010274-002), and a number of incidents cite "All" killed for bass, bluegill, catfish, crappie, etc. The frequency and magnitude of these fish kills are would not appear to be the result of direct toxic effects due to atrazine alone.

Given the low toxicity of atrazine to fish, the reason for the frequency of fish kill incidents is uncertain. About 60 percent of the reported fish kills listed under atrazine in the incident record occur during the Spring when atrazine is applied, soils are saturated and heavy rainfall is frequent. Heavy runoff may carry atrazine, other pesticides and organic loads into surface waters. The high volume and wide-spread use of atrazine increases the probability of co-occurrence of fish kills with atrazine applications. There are some other scenarios which may explain atrazine induced fish kills as well as causes unrelated to atrazine use.

Three plausible scenarios could exist in which atrazine applications may be responsible for the fish kills. First, atrazine concentrations in surface waters from runoff and/or spray drift may be much higher in shallow water adjacent to treated fields than estimated by EFED or found in monitoring studies. Second, atrazine in surface water may kill aquatic plants and the decaying process of dead plants may lower dissolved oxygen to levels too low for fish survival. Third, atrazine is known to increase the toxicity of organophosphate insecticides, such as chlorpyrifos, and a number of other pesticides which may have been applied earlier to atrazine-treated crops or applied in other fields upstream in the watershed.

Possibilities also exist that other causes, not atrazine, may be responsible for some or all of the

reported atrazine incidents. Heavy organic loads consume oxygen from the water as the organic matter oxidizes, thereby causing low dissolved oxygen levels which may cause fish to suffocate and die. Other pesticides in the watershed killed the fish as the water flowed past atrazine-treated fields. Since limited information is available in the atrazine incident records, such as water and tissue analyses, conclusions of responsibility would appear to be uncertain and the result of coincidence with little evidence for cause and effect.

The deaths of five Canada geese following an atrazine spray treatment on corn (# I008168-001) is also difficult to understand, unless atrazine was synergistic with or another corn pesticide was present, such as chlorpyrifos.

VII. Endangered Species Concerns

The Agency has developed a program (the "Endangered Species Protection Program") to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that will eliminate the adverse impacts. At present, the program is being implemented on an interim basis as described in a Federal Register notice (54 FR 27984-28008, July 3, 1989), and is providing information to pesticide users to help them protect these species on a voluntary basis. As currently planned, but subject to change as the program is developed, the final program will call for label modifications referring to required limitations on pesticide uses, typically as depicted in county-specific bulletins or by other site-specific mechanisms as specified by state partners. A final program, which may be altered from the interim program, will be described in a future Federal Register notice. The Agency is not imposing label modifications at this time through the RED. Rather, any requirements for product use modifications will occur in the future under the Endangered Species Protection Program.

Levels of Concern for Endangered species are exceeded for terrestrial plants and vascular aquatic plants. Risk quotients exceed the levels of concern for endangered terrestrial plant species from spray drift and from runoff into both terrestrial and semi-aquatic plants.

In general, risks to birds, mammals, and beneficial insects are not anticipated from direct effects of atrazine use and the levels of concern are not exceeded. However, atrazine use could have important effects on terrestrial and aquatic plants in areas adjacent to treated fields that would have indirect effects on these animals from the loss of food sources and the loss of vegetative habitat for cover, reproduction and the survival of offspring. Loss of food and vegetative habitat could force the animals to leave the affected areas and seek another acceptable habitats. Limits on acceptable habitats would increase stress on species competing for limited resources and may affect the ability to successfully reproduce and feed the young.

Acute levels of concern for endangered species are exceeded for aquatic invertebrates for all crop uses, except for the typical use rate on corn (1.1 lbs ai/A). Chronic levels of concern for

endangered species are exceeded for fish and aquatic invertebrate reproduction for all use rates, except for corn and the typical use rate on sorghum. However, Kettle et al. (1987) demonstrated severe effects on aquatic vegetation and indirect effects on fish reproduction and invertebrate populations exposed to 20 F g/L of atrazine in artificial Kansas ponds. Atrazine effects in the ponds included 60 to 90 percent reduction in vascular pond vegetation and the loss of three plant species, significant reductions in aquatic macro-invertebrate populations, a significant reduction in food consumption by adult bluegills, and a 96 percent reduction in the number of young bluegill. It is likely that reductions in the number of macro-invertebrates are due to the loss of vegetative cover to avoid predators and that bluegill young were eaten due to limited vegetative cover and the reduced availability of food (i.e., aquatic invertebrates) for adult fish species. Atrazine levels of 20 F g/L in streams and rivers are not rare occurrences and these concentrations may adversely affect aquatic vegetation, such that the loss of the vegetative habitat could affect populations of endangered aquatic invertebrates, especially crustaceans and the recruitment of young endangered fish species.

It is uncertain what effects atrazine use on crops and forests might have on vegetation in field margins and riparian areas that are necessary and important habitats for movement, cover, feeding, and reproduction for terrestrial endangered animal species, including endangered insects, amphibians, fish, birds and mammals. Riparian areas along aquatic habitats moderate water temperature and may impact the stream water quality by reducing spray drift and runoff to aquatic areas. Herbicide effects on vegetation losses in these areas may have significant effects of the suitability of these areas as habitats and food sources for endangered animal species. Reductions in acceptable habitat and limited resources are the major factors affecting many endangered and threatened species, whether they be plants, insects, clams and mussels, aquatic invertebrates, fish, birds or mammals.

Uncertainty also exists concerning the extent of atrazine effects on homing and reproduction in endangered salmon and other anadromous fish species. The laboratory study of olfactory function in mature Atlantic salmon parr and the effect of atrazine in the range of 0.5 Fg/L for sensing female hormones in urine and behavior to ground salmon skin is notable. This is so especially if the effects are significant on salmon reproduction at such a low atrazine concentration, because existing concentrations in streams inhabited by endangered salmonids may exceed this level for prolonged periods. Atrazine concentrations are likely to be their highest in the late spring and early summer following applications, at a time when salmon are returning from the ocean to spawn. It is unclear from the results of the test by Moore and Waring (1998) whether the effect on olfactory function is manifested in mature adult salmon and what effect it might have on reproduction and recruitment. These data are preliminary and additional studies are necessary to determine if there are adverse atrazine effects on adult salmon homing and adult male milt production responses to female hormones in ovulating female urine. Further study is also needed on whether those effects could be significant to reproduction and recruitment.